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AUSTENITE GROWTH IN THE INTERCRITICAL ANNEALING
OF TERNARY AND QUATERNARY DUAL-PHASE STEELS

By

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A Thesis.
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ABSTRACT

Austenite growth in the intercritical annealing of ternary (Fe-C-Mn) and quaternary (Fe-C-Mn-Si) dual phase steels is studied. The growth process is modelled assuming local equilibrium at austenite/ferrite interfaces and diffusion control. An isothermal anneal starting with a ferrite-pearlite mixture is examined. Growth proceeds in four stages: (1) austenite nucleation from pearlite (which is not examined); (2) attainment of uniform carbon activity within each austenite particle; (3) attainment of uniform carbon activity over large distances in the material (e.g., 100 µm); and (4) austenite growth controlled by diffusion of alloying element(s) in ferrite. The last stage is the only stage where significant alloying element partitioning occurs. This leads to the centre of each austenite particle retaining its initial alloying element concentration while the rim is enriched or depleted in alloying element depending on the value of the alloying element diffusion coefficient. This non-uniform concentration profile is associated with the end of austenite growth and results in a volume fraction greater than the equilibrium volume fraction. Full equilibration of the austenite does not occur in practical time periods. The preceding description applies to all cases treated. Material initially homogeneous with respect to alloying elements was
examined: (1) for a planar geometry; (2) for a spherical geometry; and (3) with different size particles. A material initially non-uniform with respect to alloy element (e.g., having an initial sinusoidal fluctuation of alloying element) was examined for the case of: (1) a wavelength comparable with spacing between austenite particles; and (2) longer wavelengths. The assumption that local equilibrium established in short times (100 s) was verified with Scanning Transmission Electron Microscope (STEM) observations. STEM and microprobe analysis data also qualitatively verified predicted Mn concentration profiles for long (50 h) anneals. Volume fractions predicted were in reasonable agreement with observed and published volume fraction data.
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CHAPTER I
INTRODUCTION

1.1 Dual Phase Steel

Dual phase steel was originally suggested by Rashid (1977) and is currently a material of commercial interest particularly for automotive applications. This interest originates from the demand for lighter more fuel efficient vehicles. A component of the total weight reduction is possible through the replacement of plain carbon steel with higher strength steel of reduced thickness. Dual phase steel is attractive for such an application since it possesses high strength while maintaining good formability.

Dual phase steel typically consists of a fine scale mixture of martensite islands in a ferrite matrix, (Rashid, 1977). In some cases untransformed austenite and bainite are also found. (Rigsbee and Vander Arend, 1979). The mechanical properties typical of, and desirable in, a dual phase steel include:

1. the absence of an upper yield point (continuous yielding behaviour); (Rashid, 1977).
2. a yield stress lower than that of other steels of comparable ultimate tensile strength; (Rashid, 1977 and Davies, 1978).
3. a high initial work hardening rate; (Davies, 1978 and Gerbase et al., 1979).
4. a high uniform elongation; (Davies, 1978, Davies and Magee, 1979).

The continuous yielding behaviour and depressed yield stress are ascribed to residual stresses resulting from the austenite to martensite transformation (although other explanations for this behaviour have been suggested, Gerbase et al., 1979). The amount by which the yield stress is decreased, increases with martensite volume fraction at low volume fractions (less than 5%) with a low yield strength to ultimate tensile strength ratio being maintained to much larger volume fractions (Rigsbee and Vander Arend, 1979). The ultimate tensile strength increases with martensite volume fraction while the uniform elongation decreases with martensite fraction. (Gerbase et al., 1979, and Davies, 1978).

As a result, the volume fraction of martensite in the steel must be selected to provide the optimal combination of these two properties. (Typically this optimal volume fraction is between 10 and 20% (Araki, et al., 1977 and Hobbs, 1977)).

There are three ways of producing a dual phase steel; (Tanaka, et al., 1979, Hobbs, 1977):

1. continuous annealing of hot or cold rolled sheet;
2. batch annealing of hot or cold rolled sheet;
3. direct production from hot rolling.

Only the first two methods will be considered here. Both continuous and batch annealing involve heating
into the intercritical (ferrite plus austenite) temperature range followed by cooling sufficiently quickly to transform the austenite to martensite. Both methods typically start with a mixture of ferrite and pearlite. (Speich and Miller, 1979).

Continuous annealing results in a relatively high cooling rate (using gas or water quenching) and as a result a lean to moderate alloy steel is used since a large amount of hardenability is not required to produce the desired martensite plus ferrite structure. The slower cooling rates associated with batch annealing necessitates a higher alloy content for the hardenability to be sufficient for producing the martensite plus ferrite structure. Typical chemistries associated with the two processes are shown in Table I.

TABLE I

Typical Commercial Dual Phase Steels
(Hobbs, 1977)

<table>
<thead>
<tr>
<th>Processing Route</th>
<th>Chemistry (wt %)</th>
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<tr>
<td>Continuous Anneal Water Quench</td>
<td>0.1% C  0.5% Mn  0.25% Si</td>
</tr>
<tr>
<td>(1000°C/sec.)</td>
<td></td>
</tr>
<tr>
<td>Continuous Anneal Gas Quench</td>
<td>0.1% C  1.5% Mn  0.3  0.6% Si</td>
</tr>
<tr>
<td>(5-20°C/sec.)</td>
<td></td>
</tr>
<tr>
<td>Batch Anneal</td>
<td>0.06% C  2.5% Mn</td>
</tr>
<tr>
<td>(0.01°C/sec.)</td>
<td></td>
</tr>
</tbody>
</table>

1.2 Objective

The relation between dual phase steel mechanical properties and volume fraction of martensite indicates that the amount of austenite formed during intercritical annealing is of
interest.

The objective of this work is to estimate the volume fraction and composition of austenite formed during the intercritical annealing period considering the effects of chemistry time and temperature. The effects of initial non-homogeneous distribution alloying element, size distribution of initial pearlite particles and the behaviour of austenite upon cooling will also be examined. The use of a ternary (e.g. Fe-C-Mn) and a quaternary (e.g. Fe-C-Mn-Si) alloy will be considered.

1.3 Local Equilibrium

A key assumption used in modelling the austenite growth is that the reaction occurs with local equilibrium existing at the austenite ferrite interface. As a consequence of local equilibrium the reaction occurs by diffusion control. (Darken, 1961 and Hillert, 1975). If local equilibrium exists then the interface concentrations correspond to the end points of a tie-line on the equilibrium phase diagram. For the binary two-phase case, this tie-line is fixed for an isothermal process. When one extends these arguments to a ternary system (with two phases at constant temperature), there is an infinite number of tie-lines from which one must be selected. The selection of tie-line is not arbitrary nor in general does the tie line describing the interface contain the bulk composition. Previous work involving applications of a local equilibrium model to ternary systems includes the study of proeutectoid ferrite growth in
Fe-C-Mn (Kirkaldy 1958, Purdy et al., 1964).

In the proeutectoid case tie-line selection was based on a mass balance, such that fluxes of manganese and carbon both gave the same expression for interface velocity. The same type of approach is followed in the current work.
CHAPTER II
CALCULATION OF ISOTHERMAL GROWTH IN TERNARY Fe-C-Mn

2.1 The Simplest Case: Initially Uniform Manganese Concentration, Planar Geometry, No Size Difference Effects.

2.1.1 Initial Conditions
In the first instance, the simplest case of isothermal austenite growth in a ternary Fe-C-Mn steel is considered. The following conditions are assumed:

1. A mixture of ferrite and pearlite is considered where the pearlite has formed without alloying element partitioning and the time to form austenite from pearlite is neglected. The former condition (unpartitioned pearlite) is to be expected for austenite stabilizing alloying elements at large undercoolings (i.e. moderate cooling rates). (Purdy, 1981, Puls and Kirkaldy, 1972). The time for austenite formation from pearlite has been observed to be less than one minute (Speich, 1981). The initial concentration profiles thus appear as in Fig. 2.1: austenite has eutectoid carbon concentration while manganese is homogeneous throughout the material.

2. A planar geometry is considered; i.e. a one dimensional diffusion problem is to be solved.

3. Effects due to differences in austenite particle size are neglected.

It should be noted that the profile in Fig. 2.1 is
symmetrical about the positions at X=0 and X=W, so that treatment of a single particle is sufficient.

The assumption of local equilibrium leads to the determination of interface compositions by equilibrium tie-lines on the phase diagram. If the distribution coefficients \( k_0, k_1, k_2 \) are known (for Fe, C and Mn respectively), then the other interface concentrations may be expressed in terms of the interface carbon concentration in the \( \gamma, C_1 \), (Hone et al., 1969) i.e.

\[
C_2^\gamma = a + b \cdot C_1
\]  

\[
C_2^\alpha = k_2 (a + b \cdot C_1)
\]

where

\[
a = \frac{1-k_0}{k_2-k_0}, \quad b = \frac{k_0-k_1}{k_2-k_0}
\]

(An explanation of notation is found in Appendix I).

To simplify subsequent calculations, the carbon concentration in the ferrite is approximated to zero and distribution coefficients are assumed not to vary with composition. They are estimated using data compiled by Uhrenius (1978) or Gilmour et al. (1972A).

The process may be considered in 3 stages. The first two stages involve carbon diffusion control, and a (consequent) negligible amount of Mn partitioning to the austenite: they are first, parabolic growth, second, a period in which carbon diffusion fields in the austenite impinge upon one another;
and last, a stage in which partitioning of the Mn from the α occurs and growth is controlled by Mn diffusion.

The second and third stages involve variable boundary conditions so that either an iterative procedure or some approximation is necessary. Here, solutions are developed using Zener's approximation (where the diffusion profile is represented as a triangle). (Zener, 1949).

Zener's approximation also provides a convenient definition for the start of the impingement stage (since such a definition is necessarily somewhat arbitrary).

2.1.2 Parabolic Growth

With quantities as defined in the carbon concentration profile, Fig. 2.2a, consideration of a bulk mass balance for carbon (neglecting the carbon content of the ferrite), gives

\[ C_1^{E_L} = C_1^{E_X_0} - 1/2 \, d \, (C_1^E - C_1^S) \]  \hspace{1cm} (2.2)

An interface mass balance involving the flux of carbon to the interface gives

\[ C_1^S \frac{dX_0}{dt} = D \frac{C_1^E - C_1^S}{d} \]

Substituting for "d" from (2.2) yields

\[ \frac{dX_0}{dt} = \frac{(C_1^E - C_1^S)^2}{2C_1^E C_1^S (X_0 - L)} \]  \hspace{1cm} (2.3)

which upon separation of variables and integrating gives the
parabolic growth rate. The value $c_1^E$ (the eutectoid carbon composition) is taken from Kirkaldy (1978). $D_1^Y$ values are from Kaufman and Radcliffe (1962).

2.1.3 Manganese Partitioning During the Initial Stage

As indicated previously, the equilibrium interface compositions are not specified "a priori" when the temperature is fixed.

The interface tie-line which determines $c_1^S$ in the above equations must be determined by equating interface velocities based on the fluxes of both carbon and manganese. Fig. 2.2b shows the Mn concentration profile associated with Fig. 2.2a. The interface manganese concentration in the austenite, $C_2^Y$, is considered to be "frozen in" as the interface advances since the diffusivity rate of Mn in austenite is two orders of magnitude lower than in ferrite. (Nohara and Hirano, 1971).

A bulk mass balance for manganese then gives

\[(X_0 - L) (C_2^Y - C_2^O) = \frac{1}{2} \frac{e}{D_2^O} (C_2^O - C_2^a) \]  \hspace{1cm} (2.4)

while the interface mass balance yields

\[ (C_2^Y - C_2^a) \frac{dx_0}{dt} = D_2^a \frac{C_2^O - C_2^a}{e} \]  \hspace{1cm} (2.5)

Combining (2.5) and (2.4) to eliminate "e" gives a velocity expression:
\[
\frac{dx_{c}}{dt} = \frac{D^{a}_{2} (c^{o}_{2}-c^{a}_{2})^2}{2 (c^{\gamma}_{2}-c^{o}_{2}) (c^{\gamma}_{2}-c^{a}_{2}) (x_{o}-L)} \quad (2.6)
\]

Equating the interface velocities in (2.6) and (2.3) gives

\[
c^{\gamma}_{2} - c^{o}_{2} = \frac{D^{a}_{2} (c^{o}_{2}-c^{a}_{2})^2 c^{E}_{1} c^{s}_{1}}{D^{\gamma}_{1} (c^{E}_{1}-c^{s}_{1})^2 (c^{\gamma}_{2}-c^{a}_{2})} \quad (2.7)
\]

which with (1), uniquely specifies the tie-line, \( s \), describing the interface compositions, and gives

\[
c^{\gamma}_{2}^{s} - c^{o}_{2} = 1 \times 10^{-5}^*.
\]

Thus austenite growth occurs here with negligible manganese partitioning, and since a finite carbon gradient provides the driving force for the austenite growth, it occurs by carbon diffusion control. The corresponding tie-line position is marked "s" in Fig. 2.2(c), i.e. \( c^{\gamma}_{2}^{s} = c^{o}_{2} \). This tie-line, of course, specifies all interface concentrations, including \( c^{s}_{1} \) the interface concentration of carbon in the austenite which is used in equations (2.2) to (2.3).

---

*For \( T = 750^oC \): \( D^{a}_{2} = 2 \times 10^{-12} \) (Nohara and Hirano, 1971, Srivastava, 1980)

\( D^{\gamma}_{1} = 1 \times 10^{-10} \) (Kaufman and Racliffe, 1962)

\( (c^{\gamma}_{2} - c^{a}_{2}) \approx (c^{o}_{2} - c^{a}_{2}) = (1 - k_{2}) c^{o}_{2} \)

\( c^{o}_{2} = 1 \) at \%, \( c^{E}_{1} = 3.25 \) at \%; \( c^{s}_{1} = 2.25 \) at \%;

\( k_{0} = 1.0297; k_{1} = 0.027, k_{2} = 0.336 \) (Uhrenius, 1978).
2.1.4 Carbon Impingement

Impingement of carbon diffusion profiles in the austenite produce the concentration profile shown in Fig. 2.3a. A carbon mass balance gives

\[ C_l^I = \frac{2LC_l^E}{x_0} - C_l^S \]

The interface mass balance gives

\[ D \left( \frac{C_l^I - C_l^S}{x_0} \right) = C_l^S \frac{dx_0}{dt} \]

which leads to

\[ 2D \frac{dA}{dt} = -\frac{1}{2} (A-x_0)^2 + 2A(A-x_0) - A^2 \ln (A-x_0) \]

where

\[ A = \frac{C_l^E}{C_l^S} \]

2.1.5 Growth with Manganese Partitioning and Ternary Interaction

After carbon has reached uniform activity throughout the material, as depicted in Fig. 2.3b the reaction will proceed under manganese diffusion control. Further growth of austenite is not possible unless the carbon concentration in the austenite is reduced from \( C_l^S \) as in Fig. 2.4a. This involves a change in interface composition corresponding to the tie-line in Fig. 2.4c moving from "S" toward "P". (The carbon content of austenite, \( C_l \), must then decrease). Since diffusion in austenite is slower than in ferrite, it is assumed that the moving interface leaves behind it a manganese profile which is a locus of equili-
brium compositions of austenite vs distance (as shown in Fig. 2.4b).

Associated with this manganese concentration profile is a slight variation in carbon concentration, such that the carbon activity is uniform. An exaggerated carbon profile is shown in Fig. 2.4d. No flux of carbon will occur if:

$$\bar{C}_1 = C_1 + R (C^\gamma_2 - C^O_2)$$  \hspace{1cm} (2.8)

$R$ is the ratio of the off-diagonal to on-diagonal diffusion coefficients. (Gilmour et al., 1972B).

Assuming the carbon concentration profile from $X_S$ to $X_0$ to be linear, a carbon mass balance gives:

$$C^O_w = \bar{C}_1 X_0 + \frac{1}{2} (C_1 - \bar{C}_1) (X_0 - X_S)$$  \hspace{1cm} (2.9)

which combined with (2.8) and (2.1) gives interface position as a function of interface carbon concentration, $C_1$. Inserting (2.8) and (2.1) into (2.9) and differentiating gives

$$\frac{dX_0}{dC_1} = \frac{\frac{1}{2} C^O_w (RE/C^S_1 - F)}{(FC_1 + RE)^2}$$  \hspace{1cm} (2.10)

where $E = a - C^O_2$, $F = Rb + 2$.

Approximating the diffusion profile of manganese in the ferrite to a triangle, the bulk mass balance for manganese may be expressed as

$$\frac{1}{2} (C^O_2 - C^O_2) e = \int_{X_S}^{X_0} (C^\gamma_2[x] - C^O_2) \, dX$$  \hspace{1cm} (2.11)
which upon combination with (2.10) and (2.1) and integration gives
\[
e = \frac{4 \, C_1^O \, L}{F^2 (C_2^O - C_2^\alpha)} \left( \frac{R_S}{C_1^O} - F \right) \left( \frac{2E}{G} - \frac{2E}{H} + b \ln \frac{H}{G} \right)
\]
(2.12)

\[G = FC_1^S + RE\]

where
\[H = FC_1 + RE\]

The interface mass balance for Mn is:
\[
D_2^a \frac{C_2^O - C_2^\alpha}{e} = \left( C_2^\gamma - C_2^\alpha \right) \frac{dx}{dt}
\]
(2.13)

Separating variables yields
\[
\frac{(C_2^\gamma - C_2^O)}{(C_2^\gamma - C_2^\alpha)} e \, dx_o = D_2^a \, dt
\]
(2.14)

(2.10), (2.14) and (2.1) yield an expression in \( C_1 \) which may be integrated numerically to give \( C_1 \) (the shift in the tie-line) as a function of time. Eq. (2.9) associates an interface position with each tie-line position while (2.13) gives interface velocity.

2.1.6 Estimation of Growth Neglecting Ternary Interaction

Neglecting the ternary interaction (i.e. the carbon profile in the austenite resulting from uniform carbon activity in the presence of a manganese gradient) simplifies the mathematics considerably.

The carbon mass balance (cf 2.9) becomes
\[ C_1^E L = C_1 x_0 \]  (2.15)

which in differential form (cf. 2.10) is:
\[ dx_0 = \frac{C_1^E L}{C_2^E} \frac{dC_1}{C_1} \]  (2.16)

The manganese concentration profile in the austenite (the locus of equilibrium compositions) then becomes (combining 2.15 and 2.16):
\[ C_2^\gamma (x) = a + \frac{b C_1^E L}{x} \]  (2.17)

Neither the bulk mass balance for manganese (2.11) nor the interface mass balance for manganese (2.13) are altered in form. However, since the expression for \( C_2^\gamma (x) \) is simplified, (2.12) becomes:
\[ e = 2(1 - C_2^O) (x_0 - x_s) + b C_1^E L \ln(x_0/x_s)/(C_2^O - C_2^O) \]  (2.18)

Fig. 2.5 compares the results of calculations with and without the effect of the ternary interaction indicating only a slight difference (typically less than 3% in interface position for a given time) when this effect is neglected. As a result the interaction is ignored in subsequent calculations. The subsequent calculations could be adjusted to account for ternary interaction by converting \( C_2^\gamma (x) \) to:
\[ C_2^\gamma (x) = \frac{2 C_1^E L - RE (x + x_s)}{(R_b + 2)x + R_b x_s} \]
2.1.7 Effect of Diffusion in Austenite on Austenite Growth

Eq. 13 only considers the contribution due to the flux in the ferrite on austenite growth. In order to obtain a better approximation it is possible to separate the total velocity \( \frac{dx_o}{dt} \) into two components:

\[
\frac{dx_o}{dt} = \left( \frac{dx_o}{dt} \right) ^a + \left( \frac{dx_o}{dt} \right) ^\gamma
\]  

\( \left( \frac{dx_o}{dt} \right) ^a \) is given by (2.13)

while \( \left( \frac{dx_o}{dt} \right) ^\gamma \) is given by

\[
\left( \frac{dx_o}{dt} \right) ^\gamma = \frac{J_2 ^\gamma}{C_2 - C_2 ^a}
\]  

(2.20)

with \( J_2 ^a \) derived from the differential of (2.17) using Fick's first law:

\[
J_2 ^\gamma = D_2 ^\gamma \frac{dC_2 ^\gamma [x]}{dx}
\]  

(2.21)

2.1.8 End of Growth

The final stages of austenite growth are depicted in Fig.2.6. Manganese diffusion fields from adjacent austenite particles impinge so that all of the ferrite suffers some depletion in manganese. If the diffusion profile in the ferrite is still approximated as linear then the mass balance for manganese (for the planar case) becomes

\[
\frac{1}{2} (C_2 ^a + C_2 ^{aI}) (W - x_o) = \int_0^{x_o} (C_2 ^\gamma [x] - C_2 ^a) \, dx,
\]  

(2.22)
where \( C_2^I \) is defined in Fig. 5b, and \( W \) is related to \( C_1^E, L \) and the bulk carbon content by a carbon mass balance:

\[
C_1^0 \cdot W = C_1^E \cdot L.
\]

Austenite growth will continue until the flux of manganese in the austenite equals that in the ferrite. This corresponds to a very shallow gradient in the ferrite because of the relatively low diffusion rate of manganese in the austenite. The manganese concentration profile associated with the end of austenite growth is shown in Fig. 2.6c.

Neglecting the slight gradient in the ferrite, makes it possible to estimate the volume fraction of austenite at the end of growth without reference to the growth kinetics. A mass balance for the Mn based on the profile in Figure 4c gives:

\[
\int_0^{X_F} (C_2^I[X] - C_2^0) \, dX = (W - X_F) \cdot (C_2^0 - C_2^a_F) \quad (2.23)
\]

A mass balance for carbon gives:

\[
C_1^E = C_1^0 \cdot W = C_1^F \cdot X_F \quad (2.24)
\]

while volume fraction, \( V_F \), is given by:

\[
V_F = \frac{C_1^0}{C_1^F} = \frac{X_F}{W} \quad (2.25)
\]

which with equations 1, 5 and 13 lead to an expression relation volume fraction \( V_F \) to bulk carbon content, \( C_1^0 \):

\[
(a-C_2^0) \cdot V_F + bC_1^0 + bC_1^0 \ln \frac{V_F}{bC_1^0 (C_2^0-a)} = (C_2^0-k_2 a) (1-V_F) - k_2 bC_1^0 (\frac{1}{V_F}) - 1 \quad (2.26)
\]
Since L and \( W \) are related by equation (2.24), the above expression for volume fraction is independent of the scale of the structure and depends only on chemistry and distribution coefficients.

However, the time to reach this volume fraction will be greater for coarser structures (and varies as \( L^2 \)). The volume fraction derived from equation (2.26) is within 1% of that calculated using the kinetic equation.

The details of the computer program used to calculate the rate of austenite growth are given in Appendix II.

2.1.9 Calculated Results

Numerical results indicate that the carbon diffusion controlled growth stages are complete in times of the order of one second. As a result, the conditions associated with Fig. 2.3b (the end of carbon diffusion controlled growth with \( X_0 = X_s \) and \( C_1 \) uniform at \( C_1^s \)) are taken as the initial conditions (i.e. at time zero) for the calculation of growth by manganese diffusion control.

Fig. 2.7 shows calculated concentration profiles for different times for an Fe-0.08% C - 1%Mn alloy annealed at 750°C. Volume fraction vs. time plots for different alloy compositions of Fe-C-Mn alloy are shown in Fig. 2.8. Volume fraction vs. time plot for an Fe-C-Mn alloy are compared with other ternarys (FeCNi, FeCSi) in Fig. 2.9.

It is interesting to note the effect of various para-
meters on the calculated results.

The reaction rate is faster for finer structures: the time to reach a given set of interface concentrations (tie-line position) varies as \( L^2 \) (the scale of the concentration profiles varies as \( L \)).

The effect of composition is shown in Fig. 2.8 where calculated results for a range of compositions in the Fe-C-Mn system are plotted. A greater concentration of alloying element leads to a greater amount of growth by alloying element diffusion. Reducing carbon content (for a given Mn content) also leads to a greater amount of growth by alloying element diffusion since the ratio of particle spacing to particle size is increased. This results in impingement of Mn diffusion fields in ferrite at a later stage of growth. If reduction of carbon content increases particle spacing with particle size constant a longer time to completion of austenite growth will result.

Both the rate and the extent of growth by alloying element diffusion are very sensitive to the alloying element distribution coefficient, \( k_2 \), and to the bulk composition of the alloying element \( C_2^0 \). As might be expected the rate is also affected by the alloying element diffusion coefficient. Elements with distribution coefficients close to unity cause less austenite growth. Further, for these elements, growth
goes to completion sooner than for elements whose distribution coefficients indicate large equilibrium concentration differences between ferrite and austenite. The combination of these effects is best illustrated by comparing the calculated results for Fe-.08%C-1%Mn and Fe-.08%C-1%Ni. Here the 1% Ni alloy \( k = .57, \ D = 2.4 \times 10^{-13} \text{ cm}^2/\text{sec.} \) alloy attains completion of austenite growth more quickly than the 1% Mn alloy \( k = .34, \ D = 2 \times 10^{-12} \) despite the fact that its diffusion coefficient is lower.

In the Fe-C-Si case (Fig. 2.9) only a small amount of austenite growth occurs, and this nears completion in times of the order of 1 second since here, a distribution coefficient close to 1 is combined with a high rate of diffusion.

2.2 Spherical Geometry

The growth rate during the third, manganese partitioning, stage was also calculated for a spherical geometry. The concentration profiles are shown in Fig. 2.10: here \( L \) is the austenite particle radius before any growth, \( r_1 \) is the radius after the finish of the carbon diffusion controlled stages, \( r_2 \) is the interface radius and \( r_3 \) is the radius of the manganese diffusion penetration into the ferrite. (Once again a linear diffusion profile is assumed.)

Spherical geometry makes the mass balances more complex. The slight variation in carbon content of the austenite associated with the manganese gradient is ignored and the carbon
mass balance becomes

\[ 4\pi C_1 L^3 = 4\pi C_1 r_2^3 \]  

(2.27)

The linear manganese profile in the ferrite from \( r_2 \) to \( r_3 \) may be written:

\[ C_2^a [r] = \frac{C_2^0 - C_2^a}{r_3^2 - r_2^2} (r - r_2) + C_2^a \]  

(2.28)

As in the planar case, (2.27) combined with (2.1) determines the manganese content of the austenite as a function of radius, \( C_2^a [r] \), so that the manganese mass balance may be written

\[ \int_{r_1}^{r_2} (C_2^a [r] - C_2^0) 4\pi r^2 \, dr = \int_{r_2}^{r_3} (C_2^0 - C_2^a [r]) 4\pi r^2 \, dr \]  

(2.29)

This equation is solved numerically to determine \( r_3 \) as a function of \( r_2 \) which allows solution of the interface mass balance similar to (2.13):

\[ \frac{D_2}{r_3^2 - r_2^2} \frac{C_2^0 - C_2^a}{r_3^2 - r_2^2} = (C_2^a - C_2^a) \frac{dt}{dr} \]  

(2.30)

The calculated profiles for different times using spherical kinetics are shown in Fig. 2.10 for a 0.08% C - 1% Mn alloy with a particle of initial radius \( L = 1 \, \mu m \).

Impingement of diffusion fields may be considered in the spherical case if the diffusion profile is again approximated as linear and the ferrite at radius \( r_4 \) is \( C_2^{aI} \). This alters the expression for the manganese concentration within the ferrite (cf. 2.24) to:
\[ C_2^a[r] = \frac{(C_2^a I - C_2^a)}{r_4 - r_2} (r - r_2) + C_2^a \]

while the upper limit of integration on the right hand side of Eq. (2.29) goes from \( r_3 \) to \( r_4 \). \( r_4 \) is related to \( C_1^c \), \( C_1^e \) and \( L \) by a carbon mass balance:

\[ C_1^c r_4^3 = C_1^e L^3 \]

(This geometrical arrangement satisfies the mass balances but does not strictly fill space).

2.3 Effects Due to Differences in Particle Size

2.3.1 Manganese Diffusion Controlled Growth

As noted above, the time to reach a given set of interface positions scales as \( L^2 \). \( L \) is the original pearlite colony half width. Thus, if austenite particles of two different original sizes are growing, the smaller particle will tend to decrease in carbon content more quickly than the larger particle. The decreased austenite carbon content is accompanied by a decreased ferrite carbon content (in local equilibrium) which results in a driving force for the diffusion of carbon in the ferrite from the larger to the smaller particle. This difference in carbon concentrations between the two particles is not associated with capillarity and such effects are neglected here. (Capillarity, of course, would tend to move carbon in the opposite direction).

Because of the low solubility of carbon in ferrite
the magnitude of the carbon gradient is small. However, this small gradient is compensated for by the high diffusion rate of carbon in the ferrite \( D^a_1 = 1.6 \times 10^{-6} \text{ cm}^2/\text{sec. at } 750^\circ C; \text{ Smith, 1962} \).

The growth rate of austenite considering carbon diffusion between particles of different size was calculated for initial conditions similar to those described in section 2.1.1 except that a particle of half width, \( L^B \) has a nearest neighbour of half width \( L^A \) (with a centre to centre distance, \( 2W \)). At the end of the carbon diffusion controlled growth stage both particles reach the same carbon concentration: \( C^s_1 \) (described earlier). Considering a flux of carbon between the two particles, \( J^a_1 \) leads to two mass balances for carbon. These mass balances relate the carbon contents of the two particles, \( C^B_1 \) and \( C^A_1 \) to the interface positions of the two particles \( X_0 \) and \( Y_0 \). The mass balance for the larger particle is:

\[
C^B_1 X_0 = C^B_1 + \int_0^t J^a_1 \, dt \quad (2.31a)
\]

and for the smaller particle:

\[
C^A_1 Y_0 = C^A_1 + \int_0^t J^a_1 \, dt \quad (2.31b)
\]

Clearly, the carbon content of each particle may not be expressed analytically as a function of interface position (as in 2.15). Rather the interface position for a given carbon content is calculated for increments of interface
position, considering the amount of carbon transferred in each time increment. The flux of carbon may be estimated by considering a linear gradient in the ferrite between the two particles:

$$J^c_1 = D^c_1 k_1 \frac{(C^B - C^A)}{2W - Y_0 - X_0}$$  \hspace{1cm} (2.32)

The size of the time increment associated with an increment of interface motion is determined by calculating the interface velocity based on the flux of manganese at each particle and is still given by (2.14). The manganese mass balance is still given by (2.11), however, $C^r_2[x]$ may no longer be expressed analytically but must be determined by combining (2.1) and (2.31) for each interface position. Appendix III gives details of the computer modelling.

2.3.2 Computed Results

Fig. 2.11 compares systems of particles of different sizes where no transfer of carbon occurs with the effect of the transfer of carbon between particles of different size. Curves A and B plot the ratio of austenite carbon contents of large to small particles in the absence of any carbon flux between the particles. Initially the austenite in the system of larger particles grows more slowly so that their carbon concentration is greater than that for the system of the smaller particles. However, the system of smaller particles reaches the end of growth sooner at which time their carbon
content becomes constant while that of the larger particles continues to decrease, eventually reaching the same carbon content at the end of austenite growth. The numerical results indicate that particles of 1μm half width would have an austenite carbon concentration 25% greater than those of 0.2μm half width in the absence of any carbon transfer between particles.

Curve C shows the results when transfer of carbon between particles of different size is considered. Comparing particles initially of 1 and 0.2μm half width, a slight difference in austenite carbon content (less than 3%) appears in times of less than a second. Thereafter, this difference decreases and is less than 0.1% in times of the order of a minute. As a result, except for very short times, the same tie-line describes approximately the interface compositions of both particles. This minute difference in carbon concentration between the particles of different sizes is maintained by a constant flux of carbon from the larger to the smaller particle throughout the austenite growth. The percentage decrease in the total amount of carbon in the larger particle

\[
\frac{C_1^B X_o}{(\frac{-E}{B E}) \frac{L}{C_1}}
\]

is shown against time in Fig. 2,12.

2.4 Austenite Growth with an Initial Non-Uniform Manganese Distribution: The Short Wavelength Case.

2.4.1 Initial Conditions:

In order to estimate the effect of an initially non-
uniform manganese distribution on austenite growth, an easily treated case is the first considered: an initial sinusoidal manganese distribution with pearlite spacing equal to the wavelength of the distribution (pearlite colonies centered on the manganese peaks). These conditions are shown in Fig. 2.13. Such conditions might be encountered for a steel cooled very slowly through the intercritical range (with nucleation and growth of pro-eutectoid ferrite commencing only in the troughs of the manganese distribution). Once again no manganese segregation is associated with the pearlite.

2.4.2 Carbon Diffusion Controlled Growth

As for the uniform manganese case, if rapid carbon diffusion controlled austenite growth is to occur with local equilibrium at the ferrite/austenite interface, a manganese spike in the ferrite must exist at the interface as shown in Fig. 2.13, and the amount of manganese partitioning must be negligible thus:

\[ C_2^I = C_2^D [X_0] \]  \hspace{1cm} (2.33)

where \( X_0 \) is interface position, and \( C_2^D [X] \) describes the initial variation of manganese concentration with distance:

\[ C_2^D [X] = A \cos \frac{nX}{W} + C_2^0 \]  \hspace{1cm} (2.34)

Since \( C_2^I [X] \) varies with position, so must the tie-line vary and as a result the interface carbon concentration, \( C_1 \), varies. Combining (2.1), (2.33) and (2.34) gives a locus of
interface carbon concentrations during carbon diffusion controlled growth,

\[ C_1[X] = (A \cos \frac{\alpha X}{W} + C_2^0 - a)/b \]  \hspace{1cm} (2.35)

Unlike the initially uniform manganese case, carbon diffusion controlled growth here proceeds with decreasing sink strength (the interface concentration increases as growth proceeds). Carbon diffusion controlled growth continues until the carbon concentration is uniform in the austenite at \( C_1^S \). Fig. 2.13 plots the locus given by (2.35) and superimposes a sequence of carbon concentration profiles during carbon diffusion controlled growth.

A mass balance for carbon is used in determining the interface position at the end of carbon diffusion controlled growth:

\[ C_1^S X_s = C_1^L \]  \hspace{1cm} (2.36)

which with (2.31) gives:

\[ (A \cos \frac{\alpha X_s}{W} + C_2^0 - a) \frac{X_s}{b} = C_1^L \]  \hspace{1cm} (2.37)

Solving for \( X_s \) and substituting in (2.36) gives \( C_1^S \).

2.4.3 Manganese Diffusion Controlled Growth

Once carbon concentration in the austenite becomes uniform at \( C_1^S \), further austenite growth must be accompanied by a decrease in austenite carbon concentration and thus a shift in the tie-line on the ternary isotherm. The relation between carbon content and interface position is identical to
the initially uniform manganese case: the carbon mass balance is given by (2.15) and the resulting manganese concentration profile at the edge of the austenite is given by (2.17).

Fig. 2.14a shows a manganese concentration profile after a short period of austenite growth by manganese diffusion control. Manganese gradients in the ferrite cause fluxes both toward the austenite and into the trough between austenite particles. This situation may not be treated as simply as previous cases (i.e. via a linear approximation of the manganese gradient) since both of the fluxes in the ferrite will be of comparable magnitude. A method of finite difference solution of the growth kinetics for these conditions is presented in a later section. However, the volume fraction of austenite at the end of austenite growth may be quickly estimated. Austenite growth will end when the manganese concentration in the ferrite is essentially uniform (at \( C_2^w \)), as shown in Figure 2.14b.

The mass balance for manganese is:

\[
\int_0^{X_s} \left( A \cos \frac{nX}{W} + C_2^o \right) \, dx + \int_{X_s}^{X_F} \left( a + b \frac{C_1^o}{x} \right) \, dx + \int_{X_F}^{X_F} C_2^w \, dx = C_2^w \frac{W}{X_F}
\]

(2.38)

This simplifies to:

\[
\frac{A}{\pi} \sin \frac{nS}{2} + C_2^o S + a(V-S) + bC_1^o \ln \left( \frac{V}{S} \right) + K_2(a+b C_1^o/V)(1-V) = C_2^o
\]

(2.39)

where \( V \) is the end point volume fraction:

\[
V = \frac{X_F}{W}
\]
and $S (= X_S/W)$ and is given by:

$$A \cos \tau S + C^0_2 - a = b \frac{C^0_1}{S}$$  \hspace{1cm} (2.40)

The end point volume fraction, $V$, determined by (2.39) and (2.40) is independent of the scale of the structure but varies with the amplitude of the initial manganese fluctuation. The end point volume fraction for this case is generally smaller than for the case of an initially uniform manganese distribution. (Of course, setting $A=0$ in (2.39) and (2.40) will recover (2.26)).

It is possible to set $V$, in (2.39) to the full equilibrium volume fraction and thus determine the amplitude of the initial manganese fluctuation necessary to have the end point volume fraction for the initial sinusoidal distribution equal the full equilibrium volume fraction. Fig. 2.14b and c show end point manganese concentration profiles for these two cases. The amplitude of the fluctuation associated with Fig. 2.14c is in most cases larger than that typically observed even in as cast alloys (where $A \leq 0.35C^0_2$, Kattamis and Flemings, 1965). This suggests that the end point volume fraction for these conditions, while smaller than for the initially homogeneous manganese case, is still larger than the full equilibrium volume fraction.

2.5 Finite Difference Calculations of Manganese Diffusion Controlled Growth

Determining the rate of austenite growth using a finite difference type of calculation makes it possible to dispense with the following two approximations:
1. that of a linear gradient in the ferrite

2. that of a constant (frozen-in) distribution in austenite.

Effects due to capillarity are still neglected.

The major advantage of the finite difference method, is that it allows the treatment of any initial manganese distribution. Situations where the growth of a single austenite particle was considered (due to symmetry of the initial conditions) were treated using a method similar to that, say of Tanzilli and Heckel (1968). A notable difference in the present treatment is that interface concentrations vary as a function of distance (determined by (2.17) and (2.1)) rather than being fixed.

The details of the finite difference calculation are given in Appendix V, while only a brief description is given here. The manganese concentration profile shown in Fig. 2.15 is divided into "K" grid points with the interface at position "R". The concentration at point \( C_I^t \) and time, \( t \), is \( C_I^t \). The finite difference expression for Fick's second law in each phase allows calculation of \( C_I^{t+1} \) from \( C_I^t \), \( C_I^t \) and \( C_{I+1}^t \). As a result (using the ferrite phase as an example) the new concentration \( C_I^{t+1} \) may be calculated between \( R+1 \) and \( K \) using the old concentrations, \( C_I^t \), and the boundary condition, \( C_R^t \) and \( C_{K+1}^t \). The boundary condition at the interface is:

\[
C_R^t = C_2^a
\]

while at \( X = W \), the boundary condition is that there
is no flux across the boundary (due to symmetry considerations), thus $C^K_i = C^{i+1}_K$. Interface velocity is given by finite difference expressions for the concentration gradient at the interface inserted into Fick's first law and (2.19)-(2.21). Interface compositions are still determined by (2.17) and (2.1).

Any manganese concentration profile (from 0 to $W$) may be used as the initial condition, so that the situation considered in section 2.4.3 may be treated. The modifications necessary for that case are noted in Appendix IV. Fig. 2.16 compares the finite difference results for austenite growth rate with results from the model described in section 2.1.6 while Fig. 2.17 compares manganese concentration profiles predicted by the two methods.

2.6 Austenite Growth in a Manganese Gradient

The situation described above (where the wavelength of the manganese fluctuation equals the pearlite colony spacing) is seldom to be encountered in practice. More typically while the ferrite grain size and spacing between pearlite colonies is of the order of 5-10 $\mu$m, the wavelength of the manganese fluctuation is of the order of 100 $\mu$m (or greater). Thus, it is worthwhile considering the behaviour of austenite particles in a situation where the manganese gradient is long relative to the particle size.

2.6.1 Initial Conditions

Figure 2.18 schematically illustrates the
initial conditions. The manganese concentration varies over a distance which is large compared with the particle size. Again, the initial conditions are austenite of eutectoid carbon concentration $C_1^E$ (the variation of eutectoid composition with Mn concentration will be ignored), with no Mn partitioning associated with the pearlite formation.

2.6.2 Carbon Diffusion Controlled Growth

It is useful at this point to summarise the tie-line positions and manganese concentration profiles associated with rapid carbon diffusion controlled austenite growth and/or shrinkage. Fig. 2.19 depicts three situations. The situation in Fig. 2.19a has been encountered already: for carbon diffusion controlled growth $C_2^\gamma = C_2^D(x_0)$. Fig. 2.19b shows a situation where carbon diffusion controlled austenite shrinkage occurs: $C_2^\alpha = C_2^D(x_0)$. Fig. 2.19c represents an intermediate case and requires Mn partitioning to move the interface. As a result the interface moves slowly and may be regarded as essentially frozen with respect to carbon diffusion controlled growth. Fig. 2.19c is a situation for austenite growth controlled by diffusion of Mn in the ferrite (since $D_2^\alpha \ll D_2^\gamma$).

Fig. 2.18 shows carbon diffusion controlled growth of an individual austenite particle situated in a Mn gradient. The initial Mn distribution $C_2^D(x)$ is given by:

$$C_2^D(x) = A_1 + B_1 x$$ (2.41)
For carbon diffusion controlled growth, the manganese concentration profile must be as in Fig. 2.19a: \( C_2^D[X_o] = \gamma \). Since manganese concentrations are different on different sides of the particle, the interface carbon concentrations also vary (as determined from the ternary isotherm, Fig. 2.18b). The carbon concentration at the right side of the particle (higher up the gradient) is lower than at the left side. Austenite growth up the gradient, at the right side of the particle occurs by diffusion with an increasing sink strength while on the left the inverse is true. Austenite growth occurs at both sides of the particle as in Fig. 2.18c until the situation depicted in Fig. 2.18d is reached. At this point, further austenite growth at the left edge of the particle may not occur since the carbon gradient in the austenite draws carbon away from the interface. Carbon diffusion controlled austenite shrinkage may not occur since the manganese concentration profile is not as in Fig. 2.19c. Rather, the flux of carbon from the interface reduces the interface carbon concentration while the interface remains effectively fixed; the manganese concentrations at the interface change to maintain local equilibrium. The sequence of concentration profiles shown in Fig. 2.18e and 2.18f are the result. Rapid carbon diffusion controlled growth of a single particle ends when the profiles shown in Fig. 2.18f are reached. Carbon concentration is uniform throughout the austenite.
particle and the same tie-line now describes the interface concentration on both sides of the particle. The manganese concentration at the right side of the particle determines this tie-line:

\[ C^Y_2 = C^D_2(X_o) \]  

while at the left side of the particle concentration "spikes" exist both in ferrite and austenite.

2.6.3 Carbon Transfer between Particles

Fig. 2.20a shows schematically the Mn concentration profile associated with two austenite particles situated in a Mn gradient at the end of carbon diffusion controlled growth. (cf. Fig. 2.18f). The particle higher up the gradient has higher interface concentrations of Mn and lower interface carbon concentration (both in ferrite and austenite). Thus, a driving force exists for carbon to diffuse from the particle low on the gradient to that which is higher on the gradient. The following analysis leads to an estimate of the time required for the carbon concentrations of the two particles to become essentially equal. Growth of austenite by manganese diffusion control will be assumed to be negligible during this period. Fortunately, the numerical results of the calculation justify this assumption. With quantities defined in Fig. 2.20a the initial carbon concentration of particle 1, \( C^{SL}_1 \), is given by combining (2.1) and (2.42):

\[ C^{SL}_1 = (A_1 + B_1 X_o - a)/b \]  

(2.43a)
\[ C_{1}^{SR} = (A_{1} + B_{1} Y_{O} - a)/b \quad (2.43b) \]

The initial total carbon concentrations of the two particles \( T_{L}^{i} \) and \( T_{R}^{i} \) are given by:

\[ T_{L}^{i} = C_{1}^{SL} X_{2} \quad (2.44a) \]
\[ T_{R}^{i} = C_{1}^{SR} Y_{2} \quad (2.44b) \]

Assuming a linear gradient of carbon in the ferrite leads to an expression for the flux of carbon between the two particles

\[ J_{1}^{\alpha} = D_{1}^{\alpha} k_{1} (C_{1}^{L} - C_{1}^{R}) / S \quad (2.45) \]

The flux of carbon in the ferrite increases the total carbon content of particle (2) at the expense of particle (1):

\[ C_{1}^{L} X_{2} = T_{L}^{i} - \int_{0}^{t} J_{1}^{\alpha} dt \quad (2.46a) \]
\[ C_{1}^{R} Y_{2} = T_{R}^{i} + \int_{0}^{t} J_{1}^{\alpha} dt \quad (2.46b) \]

The decreased carbon content of particle (1) is accommodated by decreased carbon concentration in the particle with the interfaces fixed (since neither interface has a manganese concentration profile consistent with rapid austenite shrinkage, cf. Fig. 2.19b). As a result \( X_{2} \) is constant and \( C_{1}^{L} \) is given by (2.46a). The change in carbon concentration (a shift in tie-line) is accompanied by changing interface manganese concentrations at the stationary interfaces (to maintain local equilibrium). Both positive and negative spikes are now found at both interfaces of particle (1) as shown in Fig. 2.20b.
The increased carbon content of particles (2) is accompanied by further growth of the particle. The growth occurs by motion of the interface furthest up the manganese gradient (the only interface capable of rapid austenite growth. Further motion of this interface up the gradient (with \( C_D^Y = C_D^2 [Y_0] \) causes further reduction of the interface carbon concentration. The carbon concentration is given by (2.43) with \( Y_0 = Y_1 + Y_2 \) and \( Y_2 \) given by (2.46).

The driving force for carbon diffusion will be gone when a common tie-line describes all interface concentrations, the situation shown in Fig. 2.20c.

A very large amplitude of the initial manganese fluctuation might conceivably lead to a situation where a common tie-line would have: \( C_2^\alpha > C_2^D [X_1] \). Of course, a positive spike (at the interface at \( X_1 \)) not balanced by a negative spike violates a mass balance. Before this happens a situation of the type shown in Fig. 2.19b would be reached i.e. \( C_2^\alpha = C_2^D [X_1] \) which would result in rapid austenite shrinkage at the interface lowest on the gradient. A condition necessary for this behaviour is:

\[
K_2 (A + C_2^\alpha) > C_2^\alpha - A
\]  \( (2.47) \)

where \( C_2^D [X] \) has minimum and maximum values \((C_2^\alpha-A)\) and \((C_2^\alpha+A)\), respectively.

A computer program calculating the rate of carbon transfer between two particles (with the conditions described
above is described in Appendix V. The important numerical result of the computation is that the particles have effect-
ively the same tie-line \( \frac{C_1^L}{C_1^R} = 1.01 \) in less than 100
seconds (when the spacing is 100\(\mu\)m and the manganese concentration varies from 0.65\% to 1.35\%, \(T = 750^\circ\)C). If the two
particles are both 1\(\mu\)m wide at the beginning of this stage, particle (2) will grow to 1.22\(\mu\)m as a result of taking
carbon from particle (1).

2.6.4 Austenite Growth with Manganese Partitioning

Manganese diffusion controlled growth of austenite
particles in a long manganese gradient was calculated using
a finite difference method which was basically similar to the
one used previously. The conditions taken at the beginning
of manganese diffusion controlled growth are depicted in Fig.
2.21 where three austenite particles are spaced equally
along a manganese gradient and have all interface concentrations
determined by the same tie-line as described in the previous
section. Considering the interface concentrations of mangan-
ese in the ferrite in Fig. 2.21 it is apparent that the
manganese sink strengths are similar at all interfaces. How-
ever, the manganese concentration in the neighbouring ferrite,
(the manganese source strength) is greater higher up the
manganese gradient. As a result, particles higher up the
manganese gradient will tend to grow faster by manganese
diffusion control than will the particle lower down and thus
the carbon concentration of the former particle decreases
more quickly. The difference in carbon concentration between the two particles produces a driving force for the flux of carbon from the particle low on the gradient to that which is higher. This situation has some similarity to the case treated previously where two neighbouring particles of different size were considered i.e. in both cases different growth rates determined by manganese diffusion control result in a carbon transfer between the two particles.

As for the finite difference method described earlier, the change in concentration with time at positions away from the interface is derived from the finite difference expression for Fick's second law. The interface velocity is again given by Fick's first law (and finite difference expressions for the concentration gradients at the interface). However, the derivation of interface concentrations is more complicated. Calculation of six different interface velocities \( \frac{dU}{d\xi} \), \( \frac{dV}{d\xi} \), etc.) allow calculation of six new interface positions at the end of the time increment, \( \Delta t \),

\[
U^{t+1}_0 = U^t_0 + \left( \frac{dU}{d\xi} \right)_0 \Delta t
\]  

(2.48)

The carbon mass balance for each particle must include the net flux of carbon into and out of each particle:

\[
T^{t+1}_{uv} = T^t_{uv} - J^V_{11} \Delta t
\]  

(2.49a)

\[
T^{t+1}_{wx} = T^t_{wx} + (J^V_{11} - J^X_{11}) \Delta t
\]  

(2.49b)
\[ T_{YZ}^{t+1} = T_{YZ}^t + J_{l}^{XY} \Delta t \] (2.49c)

The flux during the time increment is given by:

\[ J_{l}^{vw} = D_{l} K_{l} \left( \frac{C_{l}^{w} - C_{l}^{u}}{W_{o} - V_{o}} \right) \] (2.50)

while the carbon concentration at the end of the time increment are given by:

\[ C_{l}^{u} = T_{uv} \left( V_{o} - U_{o} \right) \] (2.51)

\[ C_{l}^{u} \] is assumed equal to \[ C_{l}^{v} \].

The expressions for the other carbon fluxes and carbon concentrations are similar in form to (2.50) and (2.51). Manganese concentrations at the interfaces are derived from the carbon concentration via (2.1). Details of the finite difference calculation are given in Appendix VI.

2.6.5 Calculated Results

Figs. 2.22 and 2.23 show a series of calculated concentration profiles for initial conditions similar to those depicted in Fig. 2.21. A sine wave of wavelength, 2W, is used as the initial manganese profile:

\[ C_{2}^{0} (x) = C_{2}^{0} - A \cos \frac{\pi x}{W} \]

As might be expected from the results of the calculation in section 2.6.3, the numerical results indicate that all interfaces are approximately described by a common tie-line (i.e.
$1.0 < C_{1}^{u}/C_{1}^{V} < 1.01$). The interfaces at $Y_{o}$ and $Z_{o}$ move quickly and the growth of this particle may be thought of as leading the system. The common tie-line raises the interface concentrations of all the particles. At times of approximately 500s $C_{2}^{u}$ is greater than the manganese concentration in the adjacent ferrite, and shrinkage of particle UV commences. This situation is shown in Fig. 2.22b although the rounding off associated with the computer graphics show the concentration at the interface and in the adjacent ferrite as being equal. The rate of shrinkage of particle UV increases, and the particle is almost entirely removed in times of the order of $2 \times 10^{4}$s (as shown in Fig. 2.23c). Note that this occurs without consideration of any effects due to capillarity.

Speich et al. (1981) has independently presented a (digital analog) calculation for manganese diffusion controlled growth of austenite. Speich's work uses fixed interface concentrations with a constant tie-line corresponding to the full equilibrium tie-line). A constant tie-line cannot simultaneously satisfy local equilibrium and a carbon mass balance. Therefore, the results of Speich's calculation are at variance with the present work.
CHAPTER III

CALCULATION OF ISOTHERMAL GROWTH OF QUATERNARY Fe-C-Mn-Si

3.1 Initial Conditions

The initial conditions are assumed to be the same as for the ternary case with both alloying elements Si and Mn of uniform concentration throughout the material at \( C^0_3 \) and \( C^0_2 \) respectively.

The addition of Si contributes another degree of freedom so that the isotherm may be represented as a tetrahedron while the \( \alpha / \alpha + \gamma \) and \( \gamma / \alpha + \gamma \) boundaries are surfaces as in Fig. 3.1a. Once again interface compositions are given by equilibrium tie-lines on the phase diagram. However, now two independent compositions must be specified to determine the tie-line. If the interface silicon concentration in the austenite \( C^\gamma_3 \) is used as an independent variable then the other interface concentrations are given by:

\[
\begin{align*}
C^\gamma_2 &= a + bC^\gamma_1 + cC^\gamma_3 \quad (3.1a) \\
C^\alpha_2 &= k_2 C^\gamma_2 \quad (3.1b) \\
C^\sigma_3 &= k_3 C^\gamma_3 \quad (3.1c)
\end{align*}
\]

where \( a = \frac{1-k_0}{k_2-k_0} \), \( b = \frac{k_0-k_1}{k_2-k_0} \), and \( c = \frac{k_0-k_3}{k_2-k_0} \).

The process may again be considered in two stages although the second stage is more complex. The first stage
involves carbon diffusion control and no partitioning of alloying elements. The second stage is controlled by diffusion of alloying elements and involves partitioning of Si and Mn.

3.2 Initial Growth

In the first stage the tie-line is fixed. Although there is an additional degree of freedom providing three unknowns: \( C_1^\gamma, C_2^\gamma, \) and \( C_3^\gamma \) (as compared with two unknowns in the ternary case). There are also three expressions for interface velocity so that the tie-line is specified.

The diffusion coefficients for Si, \( D_3^\alpha \), is still three orders of magnitude less than that for carbon, \( D_1^\gamma \), so a similar argument to that for the ternary case applies.

The concentration profiles associated with the carbon diffusion controlled stage are shown in Figures 3.1b, 3.1c and 3.1d. To arrive at the same velocity based on diffusion of all three additions, steep concentration profiles are necessary in the ferrite for both Si and Mn so that considering a mass balance for these elements gives:

\[
\begin{align*}
\dot{C}_2^\gamma &= C_2^0 \\
\dot{C}_3^\gamma &= C_3^0
\end{align*}
\]

which specifies the tie-line, i.e.:

\[
C_1^s = (C_2^\gamma - aCC_3^\gamma)/b
\]

3.3 Alloying Element Partitioning

Once the carbon has reached uniform activity throughout
the material further growth of austenite requires reduction
of the austenite carbon content from \( C_1^S \). As in the ternary
case a carbon mass balance gives \( C_1 \) as a function of inter-
face position. This is not, however, sufficient to specify
the tie-line for a given interface position.

A trajectory on the \( \alpha + \gamma / \gamma \) surface of the isotherm must
be determined by equating interface velocities based on manga-
nese and silicon diffusion.

Fig. 3.2 shows concentration profiles for manganese
and silicon after some growth with alloying elements partition-
ing. The diffusion profile in the ferrite is again approxima-
ted as linear leading to a mass balance for each element:

\[
\begin{align*}
\text{for Mn:} & \quad \frac{X^0}{X_s} (C_2[X] - C_2^0) dX = I_2 = \frac{1}{2} g (C_2^0 - C_2^a) \\
\text{for Si:} & \quad \frac{X^0}{X_s} (C_3[X] - C_3^0) dX = I_3 = \frac{1}{2} h (C_3^0 - C_3^a)
\end{align*}
\]  

(3.4)

(3.5)

Proceeding in a manner similar to the ternary, results in two
expressions for the components of interface velocity due to
flux in the austenite:

\[
\begin{align*}
\text{for Mn:} & \quad \left( \frac{dX_0}{dt} \right)_2 = \frac{D_2}{C_2^0 - C_2^a} \frac{C_2^0 - C_2^a}{I_2} \\
\text{for Si:} & \quad \left( \frac{dX_0}{dt} \right)_3 = \frac{D_3}{C_3^0 - C_3^a} \frac{0}{I_3}
\end{align*}
\]  

(3.6)

(3.7)
For both the Mn and the Si the contribution of flux in the austenite are derived and give rise to complete expressions for net interface velocity:

\[
\frac{dx_0^\gamma}{dt} = \frac{D_2}{C_2^\gamma - C_{2}^\alpha} \frac{dC_2^\gamma}{dx} \bigg|_{x=x_0} \tag{3.8a}
\]

\[
\frac{dx_0^\alpha}{dt} = \left( \frac{dx_0^\gamma}{dt} \right)^2 + \left( \frac{dx_0^\alpha}{dt} \right)^2 \tag{3.8b}
\]

\[
\frac{dx_0^\gamma}{dt} = \frac{D_3}{C_3^\gamma - C_{3}^\alpha} \frac{dC_3^\gamma}{dx} \bigg|_{x=x_0} \tag{3.9a}
\]

\[
\frac{dx_0^\alpha}{dt} = \left( \frac{dx_0^\gamma}{dt} \right)^3 + \left( \frac{dx_0^\alpha}{dt} \right)^3 \tag{3.9b}
\]

In the quaternary case, as distinct from the ternary, \(C_2^\gamma[X]\) and \(C_3^\gamma[X]\) may not be expressed analytically. Rather, the system of equations must be solved for increments of interface position. At each interface position \(C_2^\gamma\) and \(C_3^\gamma\) are determined iteratively such that the interface velocity based on the flux of manganese equals the interface velocity based on the flux of silicon, i.e.:

\[
\frac{dx_0^\alpha}{dt} = \left( \frac{dx_0^\gamma}{dt} \right)^3 \tag{3.10}
\]

As for the ternary, the mass balance equations (3.4) and (3.5) may be modified to account for impingement of diffusion fields
in the ferrite.

3.4 Computed Results

Figure 3.3 shows calculated concentration profiles for an Fe-.08%C-1%Mn-1%Si alloy annealed at 750°C for different times. Figure 3.4 shows computed austenite volume fraction vs. annealing time for this alloy and an Fe-.08%C-1%Mn ternary. The computer program which performs this calculation is shown in Appendix VII.
CHAPTER IV
COOLING AFTER INTERCRITICAL ANNEALING

4.1 Binary Case

Before considering continuous cooling, the simpler case of down-quenching to a second temperature within the intercritical range will be examined. If a binary Fe-C alloy which has reached equilibrium at a temperature in the intercritical range is down-quenched to a temperature lower in the intercritical range, the interfacial carbon content of the austenite must increase. Thus the interface is expected to respond instantly to the change in equilibrium interface concentration and the austenite to shrink rapidly as observed, for example, in hot-stage metallographic experiments (Purdy, 1978).

4.2 Ternary Case

As a first example, consider the case where the material is down-quenched just before the beginning of the manganese partitioning stage (3rd stage) of growth. The concentration profile at the time of the down-quench will be as in Fig. 2.3(b) with the interface equilibrium being determined by the tie-line "S" in Fig. 4.1. Upon down-quenching the tie-line associated with the interface concentrations must give the same interface velocity for both carbon and manganese fluxes. A severe down-quench to temperature $T_C$
(which has the $\gamma/\alpha+\gamma$ boundary marked $T_C$ in Fig. 4.1 would lead to carbon controlled shrinkage of the austenite since, at this temperature, tie-line C may be drawn to describe the interface equilibrium.

This tie-line fulfills two criteria (as shown in Figs. 4.1b and 4.1c):

1. No manganese is partitioned from the ferrite, $C_2^{a_{m}} = C_2^{o}$ (this is necessary for carbon diffusion control), and

2. The carbon content of the austenite increases, $C_1^{c} > C_1^{s}$. (This is necessary for austenite shrinkage.)

Changing the inequality in the second criterion to an equality determines a unique temperature, $T_D$, above which carbon diffusion controlled shrinkage will not occur. The phase boundary for temperature $T_D$ is shown in Fig. 4.1. The two equalities may be combined with (2.1) to give:

$$k_2^b \left( a^b + b^b C_C^{s} \right) = C_2^o$$

with $a^b$ and $b^b$ defined as in (2.1) and $k_2^b$ is associated with temperature $T_D$.

For a less severe down-quench to temperature, $T_a$, no such tie-line exists and Mn partitioning must occur. This case is depicted in Fig. 4.2. This results in finite concentration gradients of manganese in both ferrite and austenite. Since the diffusivity of manganese is greater in ferrite, continued austenite growth occurs controlled by diffusion of
manganese in the ferrite. The flux of carbon associated with the austenite growth must be of the same order as the flux of manganese so that the difference in carbon potential driving the carbon diffusion must be very small, i.e. \( C_1^\gamma = C_1^s \) which leads to the tie-line, a, describing the interface equilibrium at temperature \( T_a \).

The temperature difference \( (T_s - T_b) \) between carbon controlled austenite growth and carbon controlled ferrite growth represents a hysteresis which is closely analogous to that noted by Hillert (1968) in terms of the carbon activities associated with non-partitioned ferrite growth and austenite growth at a given temperature.

A trajectory of the austenite interface compositions as the material is cooled through the \( \alpha + \gamma \) range is shown in Fig. 4.3. Manganese controlled growth occurs as the temperature drops from \( T_s \) to \( T_b \) with the carbon content of the austenite essentially constant. At temperatures below \( T_b \) carbon controlled shrinkage occurs. Trajectory \( b' \) is not a straight line but the locus of points generated at different temperatures by tie-lines having \( C_2^\alpha = C_2^o \).

Figure 4.1c depicts the concentration profile associated with carbon diffusion controlled shrinkage. \( C_1^c \) is given by

\[
C_1^c = \frac{(C_2^o/k_2-s)}{b}
\]

Using the same method as was used to calculate the parabolic growth rate, the shrinkage distance, \( Y \), is given by
\[ Y = \left( C_l^C - C_s^C \right) \left( \frac{D_{1t}}{C_s^C} \right)^{1/2} \]

This gives a rough estimate of the shrinkage rate at a given temperature.

If the alloy is held at \( T_s \) long enough for appreciable manganese partitioning to occur, i.e. the interface tie-line shifts from \( s \) to \( t \) in Fig. 4.4 and the Mn concentration profile is as in Fig. 2.4b, the situation is more complex.

If austenite shrinkage occurs by reverse motion of the original austenite/ferrite interface then three ranges of temperature must be considered:

Shrinkage of the austenite, at the original ferrite-austenite interface and with no manganese partitioning is shown in Fig. 4.4 and will occur at temperatures below \( T_g \) (e.g. \( T_g' \)) where tie-line \( g' \) may be constructed such that \( C_2^a = C_2^t \) and \( C_1^a > C_1^t \). As shrinkage proceeds (with the sequence of concentration profiles for Mn shown in Fig. 4.4b) the tie-line shifts towards \( ee' \) as \( C_2^a \) values decreases following the concentration profile produced at the annealing temperature \( T_s \).

Temperatures greater than \( T_g \) require manganese partitioning for interface motion to occur, and thus a much lower shrinkage (or growth) rate results. The shrinkage with manganese partitioning requires manganese diffusion control and a minute difference in carbon potential, i.e. at temperatures greater
than \( T_g \) the interface concentration of carbon in the austenite is approximately equal to \( C_1^t \). Two temperature ranges result separated by temperature \( T_e \), which has a tie-line such that \( C_1^e = C_1^t \) and \( C_2^e = C_2^o \).

Temperatures above \( T_e \), for example \( T_d \), shown in Fig. 4.5, have \( C_2^e < C_2^o \) so that austenite growth continues controlled by diffusion of manganese in the ferrite.

Temperatures between \( T_e \) and \( T_g \), e.g., temperature \( T_f \) shown in Fig. 4.6 have \( C_2^e > C_2^o \) which leads to austenite shrinkage. As may be seen in Fig. 4.6b both the flux in the austenite and the flux in the ferrite contribute towards interface motion in the shrinkage direction:

\[
\frac{dX}{dt} = \frac{-1}{C_2^{\gamma f} - C_2^{\alpha f}} \left( |J_2^\alpha| + |J_2^\gamma| \right)
\]

Carbon diffusion controlled austenite shrinkage is expected to occur at temperatures just below \( T_e \) if and when the ferrite penetrates the manganese-enriched part of the austenite particle to reach the non-enriched centre. The limitation here is, of course, that ferrite must actually penetrate or nucleate inside the manganese-enriched periphery. Because the austenite in the manganese enriched regions is stabilized with respect to ferrite growth, a structure composed of a ferrite matrix containing shells of martensite which, in turn have ferrite centres may result upon cooling.
CHAPTER V

EXPERIMENTAL METHODS AND RESULTS

5.1 Sample Preparation

Samples of the experimental steels (see Table II) were sealed in quartz tubes under vacuum, homogenized by annealing at 1200°C for 7 days, then water quenched. The grain structure was refined by five cycles of re-austenitizing and quenching (Grange, 1966). Finally, a re-austenitizing treatment was followed by air cooling to produce a ferrite-pearlite structure. No banding was observed after this treatment.

Intercritical annealing for periods less than $1.5 \times 10^4$ s was done in a salt bath equipped with an electric stirrer. Longer intercritical anneals were done in a box furnace after sealing the specimen in a vycor tube under vacuum. Temperature error was estimated as $\pm 1 \degree C$ in the box furnace and $\pm 2.5 \degree C$ in the salt bath.

5.2 Quantitative Metallography

Metallographic specimens were examined in a Quantimet Image Analyser in order to determine the volume fraction of martensite. The field examined by the Quantimet consisted of a square of 400 x 400 "picture points" each of which was a 0.42 \( \mu \)m square. Quantimet output for a given
<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.056</td>
<td>0.97</td>
<td>0.001</td>
<td>0.005</td>
<td>0.011</td>
<td>0.042</td>
</tr>
<tr>
<td>B</td>
<td>0.079</td>
<td>0.99</td>
<td>0.001</td>
<td>0.004</td>
<td>0.009</td>
<td>0.040</td>
</tr>
<tr>
<td>C</td>
<td>0.300</td>
<td>0.97</td>
<td>0.001</td>
<td>0.005</td>
<td>0.008</td>
<td>0.041</td>
</tr>
</tbody>
</table>
field included:

1. the number of discrete particles in the field;
2. the number of picture points in the field which were in the second phase (the area output);
3. the number of picture points in the field which contained the interface between phases (the perimeter output).

Since the microstructure was inhomogeneous, 25 fields were examined for each specimen. The volume fraction shown in Figs. 5.1 - 5.3 are the average area fractions over the 25 fields while the error bars correspond to $\pm \sigma$, the standard deviation. Systematic errors in Quantimet analysis may result from improper identification of phases, i.e. identifying regions of martensite as ferrite and vice versa. Correct identification of the phases present depends upon the combination of adequate contrast in the specimen (produced by etching) and the proper selection of discriminator grey level (i.e. the light intensity below which the Quantimet identifies a darker second phase).

Increasing etching time darkens the martensite but also introduces other dark features, e.g. etch pits and ferrite grain boundaries. However, the quantimet may be adjusted to exclude features smaller than a particular size (e.g. 4 picture points). This capability reduced the number of ferrite grain boundaries counted in an over-etched specimen. If the
etchant attacks the ferrite immediately adjacent to the interface, the second phase may appear enlarged leading to a systematic overestimate of its volume fraction. This overestimate will be proportional to the perimeter of second phase and thus proportional to the perimeter output of the quantimet. If the extra area associated with the attack of ferrite near the phase boundary is assumed to be one picture point (0.42μm) wide, then the total extra area expressed as an area fraction will equal the perimeter output divided by the total number of picture points. Typical perimeter outputs expressed in this manner are shown in Fig. 5.1 to 5.3.

The etching generally made the outer edge of the martensite darker than the centre so that the centres of some large martensite particles were some times excluded from the area fraction count. The sensitivity of the measured volume fraction to etching and discriminator setting is illustrated in Fig. 5.1 which includes points plotted for a lower discriminator setting. Fig. 5.3 includes a point where the specimen was clearly under-etched. Etching was timed and discriminator levels were kept constant in order to be as consistent as possible.

The observed volume fractions are compared with calculated volume fractions in Fig. 5.1 to 5.3. The calculated volume fractions are for a spherical geometry, calculated with two different sets of thermodynamic input
data. Calculations for a planar geometry are also included. The radius of the original pearlite colony (noted in the Figure caption) was estimated by optical examination of the initial microstructure. (Note that these structures are appreciably coarser than typical commercial structures which have colony radii of the order of 0.5μm, Speich, 1981).

5.3 Electron Microprobe Analysis

A sample was annealed for 50 h at 750°C and prepared for examination in a CAMECA electron probe microanalyser. The electron microprobe may be focussed to a spot size of approximately 1μm, a distance comparable to the width of the predicted concentration profile (cf. Fig. 2.7). To account for the relatively large volume of material being sampled by the probe, the predicted concentration profile may be convoluted with a function which describes the spatial distribution of the probe intensity. The convolution generates a concentration profile which one expects to observe using the electron microprobe. The convolution technique used was similar to that used by Gilmour (1970). The actual concentration profile C(X) is related to the observed concentration profile F(X) and a probe function G(X) by:

\[ F(X) = \int_{-\infty}^{\infty} C(X') G(X-X') \, dX' \]

The probe function was assumed to be Gaussian:

\[ G(X) = \frac{1}{2d} \exp \left( -\pi \frac{X^2}{2d^2} \right) \]

The parameter "d" characterizing the Gaussian was
determined by performing a step scan across a step function. The step function was made by electro plating pure iron on homogenized alloy B. The details of this procedure are given in Gilmour (1970).

The computer program which performs the convolution is described in Appendix VIII.

In order to remove effects due to surface relief, (produced by etching) the sample was examined in the as-polished condition. As a result the microstructure was not visible during microprobe examination, and martensite particles had to be located by changes in the intensity of MnKα x-rays (i.e. the chart output of the microprobe). Etching, marking with a micro-hardness indenter and taking photo-micrographs before re-polishing and after microprobe examination made it possible to locate large particles for microprobe examination. The series of photomicrographs in Fig. 5.4 trace this sequence. Particles which appear large in the metallographic section are the most likely to be sectioned through their centre thus minimizing the sectioning effects which are illustrated schematically in Fig. 5.5.

Fig. 5.6 and 5.7 each show a predicted concentration profile, a predicted microprobe concentration profile (i.e. a convolution of the predicted concentration profile) and observed microprobe results. The profile in Fig. 5.6 was produced by scanning across the particle indicated in Fig. 5.4 while the profile in Fig. 5.7 is from a random micro-
probe scan and, as a result, shows poorer fit due to sectioning effects.

5.4 **STEM Microanalysis**

Thin foils were prepared and examined using two types of scanning transmission electron microscope (STEM) in order to observe the manganese concentration profiles present (the VG HB5 STEM and the Phillips 400 TEM/STEM).

A schematic diagram of the HB5 STEM x-ray detection system is shown in Fig. 5.8. Manganese concentrations were determined from spectra produced by energy dispersive x-ray analysis (EDAX). To accurately observe concentration profiles on such a fine scale it is desirable to:

1. optimize the spatial resolution of the probe used;
2. maximize the intensity of characteristic x-rays produced by the sample;
3. minimize the intensity of non-characteristic x-rays.

5.4.1 **Non-Characteristic X-rays**

There are two sources of non-characteristic x-rays:

1. **continuum x-rays**: (generated by the probe in the sample);
2. systems background: x-rays generated by radiation (both stray electrons and hard x-rays) not contained in the probe.

The intensity of x-rays from both these sources are (with one exception) insensitive to microscope operating conditions.
Specifically, the relative intensity of continuum x-rays decreases with the angle between the x-ray detection and incoming electron beam, while systems background is reduced through collimation of both the x-ray detector and incident electron beam (Goldstein, 1979). Insertion of the selected area aperture during analysis also acts to collimate the incident electron beam (this is the exception noted above).

5.4.2 Spatial Resolution and Sectioning Effects

It is not possible to observe a manganese concentration profile which indicates the actual variation of Mn concentration in a line normal to the austenite/ferrite interface for three reasons:

1. The electron probe at the entrance surface of the foil has a finite diameter (the spot size). This is the limiting probe diameter for very thin foils.

2. Beam spreading occurs within the specimen which results in a further increase in probe size as it travels through the foil (reaching a maximum at the foil exit surface).

3. Sectioning effects result in the interface being inclined to (rather than parallel to) the electron beam. While not actually increasing the probe size this effectively decreases the spatial resolution of the probe.

4. Specimen Drift: motion of the specimen relative to
the probe while acquiring x-rays.

5.4.3 **Spot Size**

Spot size may be estimated using the method of Wells (1974) and Venables and Janssen (1980): contributions due to chromatic, spherical and diffraction aberrations plus geometric diameter (source size) are added in quadrature. Estimates of spot size produced on the McMaster HB5 STEM have been tabulated by Robertson (1981) for different operating conditions. The 200μm virtual objective aperture (VOA) was used on the McMaster STEM and produces a spot size of \(90\AA^\circ\). The smallest VOA results in a smaller spot size but is not used as it leads to a reduced x-ray signal. Further, it will be shown below that the spot size is not the major limitation on the spatial resolution.

5.4.4 **Beam Spreading**

Goldstein (1979) gives an expression for beam spreading in the specimen:

\[
b = 625 \frac{Z}{E} \left( \frac{\rho}{A} \right)^{\frac{1}{2}} t^{\frac{1}{2}}
\]

(5.1)

which gives \(b = 200\AA\) for \(t = 1000\AA\) (for pure Fe, \(E = 100\)kV; \(t\) is thickness. \(A\) is atomic wt. \(Z\) is atomic number). Beam spreading, rather than spot size limits the spatial resolution of the probe for typical thin film specimens.

5.4.5 **Sectioning Effects**

As with the electron microprobe, because a finite volume of material is sampled by the probe, there is a
difference between the observed concentration profile and the actual concentration profile. The observed concentration profile will generally be broadened while the absolute heights of concentration peaks will be diminished. Sectioning effects, for the most part will amplify these effects, as shown below.

5.4.5a Broadening of Peaks

Fig. 5.9 shows three situations where a planar interface (or any set of parallel planes of equal concentration) is inclined to the electron beam by an angle $\phi$. A concentration profile along XX' might for example be as shown in Fig. 5.9d.

Fig. 5.9a shows peak broadening occuring even for a probe of infinitesimal diameter: peak width would increase from $W$ to $PP'$ where:

$$PP' = W/\cos \phi + t \tan \phi$$  \hspace{0.5cm} (5.2)

The interface would appear to have a thickness of $t \tan \phi$.

In Fig. 5.9b, where the spreading of the probe in the material is approximated to a conical distribution of semi-angle, $\theta$, (and $\theta < \phi$) the change in profile width is from $W$ to $QQ'$:

$$QQ' = t(\tan \phi + \tan \theta) + W/\cos \phi + S$$  \hspace{0.5cm} (5.3)

Fig. 5.9c is similar to 5.9b but $\phi > \theta$ and the change in profile width is from $W$ to $RR'$:

$$RR' = W/\cos \phi + 2t \tan \theta + S$$  \hspace{0.5cm} (5.4)

5.4.5b Peak Height

The observed concentration for a given probe position
is related to the range of concentrations sampled by the probe. This range of concentrations is determined by the projection of the probe on a line normal to the iso-concentration planes, $P$.

For the case depicted in Fig. 5.10a the projection along $XX'$ is given by:

$$P = t \sin \phi$$  \hspace{1cm} (5.5)

Assuming a uniform intensity distribution of x-rays generated within the concentration range sampled allows a rough estimate of the effect on the resulting peak height. The observed peak height becomes the maximum average concentration in a region of width $P$ on the actual concentration profile. For the case in Fig. 5.10d (a linear concentration profile) the observed peak height $C_2^\gamma$ becomes reduced to $C_2^{\gamma*}$ where

$$C_2^\gamma - C_2^{\gamma*} = \frac{m}{2} P$$  \hspace{1cm} (5.6)

where $m$ is the slope of the concentration profile.

Fig. 5.10b and c consider a conical probe. When $\phi > \theta$, $P$ is given by:

$$P = (S + t \tan \theta + t \tan \phi) \cos \phi$$  \hspace{1cm} (5.7)

When $\phi < \theta$, $P$ is given by:

$$P = (S + 2t \tan \theta) \cos \phi.$$  \hspace{1cm} (5.8)

For this case, ($\phi < \theta$) the probe actually samples a smaller range of concentrations than it would if the interface were normal to the beam, i.e. when $\phi = 0$: 
P = S + 2t \tan \theta. \quad (5.9)

5.4.6 **Specimen Drift**

Concentration profiles were produced by moving the probe with the specimen fixed. The probe was located at known distances along a line perpendicular to the martensite-ferrite interface by attaching a section of ruler to the CRT screen. Motion of the image was measurable and of the order of 0.1\mu m in times of the order of 1h. Thus, a specimen drift of approximately 30% might be expected in 100s of acquiring x-rays. This drift further reduces spatial resolution.

5.4.7 **Characteristic X-rays**

The statistical error associated with n counts for a characteristic x-ray peak is approximated as $\sqrt{n}$. Thus the relative error in a given analysis time is reduced by maximizing the count rate. However, there are limitations imposed by the detection system which produced undesirable effects at very high input count rates. The sources of these limitations are detailed in Woldseth (1973). A reduction in energy resolution and a shift in peak energies occurs at high count rates. Further, at high input count rates the percentage dead-time increases which decreases the output yield of the detector (i.e. number of output counts/number of input counts). As a result the maximum desirable count rate typically gives a dead-time between 40 and 60%.

The count rate may be altered by changing the VOA.
As noted above, this does not produce an appreciable difference in spatial resolution of the probe.

5.4.8 X-ray Absorption

Absorption of x-rays by the specimen reduces the intensity of x-rays entering the detector and may also alter the ratio of characteristic x-ray intensities. A modification of the Cliff-Lorimer approximation which includes an absorption correction is given by Goldstein (1979) and is of the form:

\[
\frac{C_{Mn}}{C_{Fe}} = K_{FeMn} \frac{T_{Mn}}{T_{Fe}} R
\]  

(5.10)

(the Cliff-Lorimer approximation sets \( R = 1 \)). Table III summarizes the absorption correction for different operating conditions.

<table>
<thead>
<tr>
<th>Intensity Ratio</th>
<th>Tilt Condition</th>
<th>Take-off Angle</th>
<th>Thickness</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{MnK}^\alpha : \text{Fe K}^\alpha )</td>
<td>Full specimen tilt</td>
<td>42°</td>
<td>5000Å</td>
<td>1.0053</td>
</tr>
<tr>
<td>( \text{MnK}^\alpha : \text{Fe K}^\alpha )</td>
<td>No specimen tilt</td>
<td>15°</td>
<td>5000Å</td>
<td>1.014</td>
</tr>
<tr>
<td>( \text{ArK}^\alpha : \text{Fe K}^\alpha )</td>
<td>No specimen tilt</td>
<td>15°</td>
<td>5000Å</td>
<td>.71</td>
</tr>
</tbody>
</table>

The \( \text{ArK}^\alpha \) case is considered to illustrate the effect of high absorption conditions (i.e. low take-off angle and large thickness) on the rest of the x-ray spectrum. The \( \text{MnK}^\alpha / \text{FeK}^\alpha \) ratio is largely unaffected by absorption since their mass absorptions coefficients are similar. However, continuum x-rays
of lower energy will suffer; e.g. similar to the ArKα energy of 2.95KeV more absorption and change the appearance of the x-ray background. Operation of the STEM when the tilt drives were inoperable actually changed the sign of the slope of the background intensity in the spectrum (i.e. instead of background decreasing with increased energy the reverse was true). To reduce effects due to absorption, specimens were examined at maximum tilt (i.e. maximum take-off angle).

5.4.9 **Interpretation of STEM Data**

5.4.9a **Background Subtraction**

The weight fraction of manganese may be estimated from the x-ray spectrum data using the Cliff-Lorimer approximation:

\[
\text{wt} \% \text{Mn} = \frac{\text{Mn-Fe}}{\text{Gross Mn} - \text{Background Mn}} \times \frac{\text{Gross Mn} - \text{Background Mn}}{\text{Gross Fe} - \text{Background Fe}}
\]  

(5.11)

Since the background Mn was typically 50% of the gross Mn, it was important to reduce any error in the background estimate. Sources of error in the background estimate are:

1. A statistical error which may be reduced by maximizing the number of counts used to estimate background (in a given spectrum).

2. An extrapolation error resulting from estimating the background Mn from other regions of the spectrum. Statistical errors and errors introduced by the presence of trace elements contribute to this error.
The extrapolation error was reduced by using as much data as possible in performing the extrapolation. A linear regression was performed using data from all spectra produced with the same operating conditions.

The total number of counts from the four windows in Fig. 5.11 were determined. These windows avoid the FeKα and FeKβ Si escape peaks. Windows are not set to the right of the Mn peak since any background to the right of Fe absorption edge is reduced by absorption in the Fe.

The background per channel (total background in window-number of channels in window) for each window was normalized by dividing by the total number of counts in all four windows. The normalized background per channel v.s. energy relationship will be the same for all spectra (for a given set of operating conditions) if the form of this relationship is independent of the size of the spectrum (i.e. independent of the counting time and count rate for the range of count rates used). This will not be true if the amount of absorption is sufficiently large since (as noted previously) low energy background will suffer more absorption than background immediately below the FeKα peak. Fig. 5.12 plots B1/B4 (defined in Fig. 5.11) for a range of count rates and suggests that this absorption effect may be neglected for the range of thicknesses typically encountered. The count rate increases with specimen thickness and the absorption effect on background would appear as a decrease in the B1/B4 ratio at high count rates.
However, Fig. 5.17 suggests that a slight change in the form of the background vs. energy relation may result from different absorption conditions. The set of points with the higher concentration results from performing the background linear regression using only the 19 spectra produced from the sample associated with Fig. 5.17. The other set of points results from performing the background linear regression using data from 55 spectra: those associated with the concentration profile in Fig. 5.17 plus those associated with the concentration profile in Fig. 5.18. The difference between the two sets of points is small compared with the statistical error. Further, there is no qualitative difference in the two concentration profiles with one being slightly translated with respect to the other. Applying an internal standard as described in the following section will remove the difference altogether.

5.4.9b Application of Standards

The Cliff-Lorimer constant $K^{Mn-Fe}$ in (5.11) has been calculated to be 0.96 and experimentally observed to be 0.985 (Goldstein, 1979). Fig. 5.13 shows an observed concentration profile (with $K^{Mn-Fe}$ set equal to 1) produced on the Cavendish HB5 STEM. Because of the homogenization treatment and short intercritical anneal the material away from the martensite/ferrite interface was considered suitable as an internal standard (and assumed to have the bulk manganese concentration of 1 wt %). The observed concentrations are consistently
higher by approximately 0.2 wt%. The same shift was observed in two other concentration profiles produced on the same instrument from different specimens (i.e. different regions of the material). Such a large shift in concentration cannot be removed by applying a reasonable Cliff-Lorimer constant. Most of the observed shift in the concentration may then be explained by the presence of part of the low energy tail of the FeKα peak in the Mn window. Specifically, 0.2% of the total FeKα peak in the manganese window would result in the 0.2 wt% upward shift of the observed result.

Without reference to a pure Fe standard spectrum produced on the same detection (or at least a sample with a large amount of Fe and no elements present to produce characteristic x-rays in the Mn window) it is not possible to determine relative magnitude of the two contributions to the concentration shift described above.

The method of division of the concentration shift has little effect on the resulting concentration profiles. Fig. 5.14 and 5.16 have $K_{MnFe}$ = 1 with all the 0.2% shift ascribed to "tailing". Assuming $K_{MnFe}$ = .985 with tailing of 0.185 would leave concentrations near 1 wt% in these figures unaffected while reducing the peak height in Fig. 5.14 from 1.5 to 1.49.

Concentration profiles in Fig. 5.15, 5.17 and 5.18 show data with no standardization (i.e. only the ratio of
net Mn/Fe counts is plotted). A downward shift (of approximately 0.1 wt%) would improve the fit of the McMaster HB5 STEM data slightly.

5.5 Cooling Behaviour

A specimen was annealed for 6 days at 800°C, slow cooled for approximately 5 seconds, then water quenched. A photomicrograph of the resulting structure is shown in Fig. 5.19. Note that many of the martensite particles have ferrite cores, which is consistent with the behaviour suggested in Section 4.2.

* Quantimet Image Analyser, HB5 STEM and Phillips 400 are brand names of commercially available instruments.*
CHAPTER VI

DISCUSSION

For clarity the discussion of this work is subdivided into sections dealing with:

1. Experimental Results
2. Computer Modelling

6.1 Experimental Results

6.1.1 Volume Fraction Prediction

A number of sources of error associated with the Quantimet volume fraction data have been discussed in Chapter V. With these in mind, the experimentally observed volume fraction data show reasonable agreement with the predicted volume fraction data, i.e., the end point volume fractions are within experimental error of those predicted and the times to completion of austenite growth are of the same order as those predicted. Fig. 6.1 shows predicted volume fraction data compared with that observed by Srech (1981). The agreement in this case is similar.

The observed volume fractions for short times are consistently lower, presumably for the following reasons:

1. The length of time of the intercritical anneal is an overestimate of the length of times during which austenite growth is occurring. The time for the
specimen to come to temperature plus the time to nucleate austenite from pearlite must be subtracted from the length of the intercritical anneal to arrive at the time available for austenite growth.

2. The very rapid early stages of austenite growth (by carbon diffusion control) may be slowed by interface control of the reaction.

The difference in volume fraction at the end of growth assuming the measured volume fractions are perfectly accurate could be ascribed to inaccuracies in the input thermodynamic data. The sensitivity of the calculated results to differences in thermodynamic data is shown in Figs. 5.1 to 5.3.

The quality of volume fraction data could be improved in the following ways:

1. Use of an interactive system would aid in the proper identification of the phases counted.

2. A system with a higher spatial resolution could improve accuracy and would reduce the magnitude of the error associated with phase boundaries (perimeter output). The spatial resolution of the counting system is of interest here and may not be limited by the optical resolution, i.e., increasing the magnification of the optical microscope used could lead to enhancement of the counting system resolution.

Calculated austenite volume fraction data was compared with austenite volume fraction data observed by Garcia and
DeArdo (1979). The observed data, in this case, was consistently lower than predicted. This is probably due to the fact that some carbides remained untransformed throughout the intercritical anneal. The intercritical anneal, at 725°C, was not far above the eutectoid temperature and the carbides may have initially been segregated with respect to alloying elements.

6.1.2 STEM Results

Concentration profiles observed both with the STEM and the microprobe are qualitatively in good agreement with calculated concentration profiles. The observed STEM concentration profiles for short times (Figs. 5.16 and 5.17) support an assumption central to the theoretical treatment, i.e., it is clear from these experimental observations that local equilibrium is established even in short times. A para-equilibrium (Gilmour et al. 1972a) condition does not describe the martensite/ferrite interface since the absence of any manganese partitioning is necessary for (indeed a definition of) para-equilibrium.

The observed concentration profile at long times (Fig. 5.18) also support the theoretical model: clearly a tie-line shift has produced an increased peak manganese concentration (of the right order) while the centre of the martensite has experienced no manganese partitioning. A precise quantitative measurement of peak Mn concentration (and consequently measurement of the distribution,
co-efficient for manganese) is not possible here for the following reasons:

1. The effects of a finite probe diameter and of sectioning effects on the observed peak height have been shown to increase with the slope of the actual concentration profile (cf Section 5.4.5).

2. An absolute concentration figure requires both a pure Fe standard and a standard Fe-Mn alloy of known composition.

3. Even if the above conditions are satisfied the accuracy of observed concentrations figure in this range of concentration (near 1 wt.%) becomes limited by the statistical reliability of the data.

The STEM data's reliability requires that the variation in observed concentrations is greater than the error associated with the concentration measurements. The magnitude of the statistical error at the low concentrations measured approaches the value of the minimum mass fraction detectable (MMF). Both are dependent on the peak (background ratio (P/B). Ziebold (1967) gives an expression for MMF:

\[ \text{MMF} = 2.33 (P/B \cdot P \cdot \tau)^{-1/2} \]

Approximating the material as pure Fe gives MMF of the order of 0.10% in 100 seconds (when P/B = 90, P \cdot \tau = 40,000).

Other contributing errors are relatively unimportant.
Absorption has little effect on the observed intensity ratios (because the mass absorption coefficients for MnKα and FeKα x-rays are similar). The effect of x-ray absorption on the form of the background (and subsequently the background subtraction technique) has been shown to be small (cf. Fig. 5.17).

6.1.3 Microprobe Results

The electron microprobe results show qualitative agreement with those predicted after the resolution of the microprobe are compensated for via a convolution technique. The spatial resolution of the probe precludes any quantitative estimate of the manganese segregation although the lack of manganese enrichment in the centre of the austenite is observed. The statistical error associated with the probe results is much smaller since the energy resolution of the wavelength dispersive system is superior and results in a higher peak/background ratio.

6.2 Calculated Results

6.2.1 Method of Calculation

The calculated results using a linear approximation of the diffusion gradient and assuming a frozen profile in the austenite are virtually identical to the results of the finite difference method where these approximations are avoided. The former method yields a more transparent result and requires much less computer time.
6.2.2. Stages of Growth

Isothermal austenite growth during intercritical annealing of a ternary ferrite pearlite mixture occurs in a sequence of four stages:

1. Nucleation of austenite from pearlite (which has been noted in other work as occurring in times less than one minute; (Speich, 1981)).

2. Attainment of uniform carbon activity over short distances (distances of the order of 10 μm, i.e., the ferrite grain size) which takes place in times of 1–10 seconds after nucleation. This corresponds to uniform carbon activity throughout the material if the material does not have initial variations of alloying element concentration over long distance.

3. Attainment of approximately uniform carbon activity over long distances, e.g., 100 μm takes place in times of approximately 100 s (at 750°C). Particles high on a manganese gradient grow during this stage as the carbon concentration of particles low on the gradient decreases (without the latter particles shrinking).

4. Austenite growth controlled by diffusion of alloying element in ferrite. This is the only stage where partitioning of alloying element occurs. The central region of each austenite particle will
be unpartitioned while the rim will be enriched or depleted in alloying elements (depending on the value of the individual alloying elements' distribution coefficients).

Since the volume fraction of martensite/austenite is vital in determining the work-hardening response and strength of the material, the prediction of the rate of austenite growth is a central objective of this work. The ternary case can be understood with the aid of Figs. 2.4 and 2.6 which demonstrate that the slow alloying-element-controlled growth is accompanied by the steady variation of the interfacial equilibrium compositions. This variation is of course possible using a ternary analysis but does not arise in a pseudo-binary approximation treatment.

An analogy may be drawn between γ growth by alloying element partitioning in the ternary case and classical non-equilibrium freezing for a binary system. The ternary Fe-C-Mn isotherm may be drawn as in Fig. 6.2 if chemical potential of carbon is substituted for carbon concentration. Carbon chemical potential then becomes analogous to temperature in the binary case. In each case, the rate of transport in the growing phase is much less than that in the consumed phase. In each case, the concentration profile "frozen" into the growing phase is a locus of interface equilibrium concentrations. In the binary freezing case the change in interface composition, \( C_L \), is related to mass fraction solidified \( (1 - M_L) \) by considering a mass balance.
with the well-stirred liquid:

\[ M_L \frac{dC_L}{dt} = -C_L (1 - k) \frac{dM_L}{dt} \]  

(6.1)

In the ternary austenite growth case the interface composition of carbon is related to the austenite mass fraction, \( M_f \), via a mass balance for carbon:

\[ C_L = \frac{C^0_L}{M_f} \]  

(6.2)

Differentiating gives:

\[ (M_f)^2 \frac{dC_L}{dt} = -C^0_L \frac{dM_f}{dt} \]  

(6.3)

Manganese concentration is then related to carbon concentration by the phase diagram (2.1).

In the freezing case, growth of a pro-eutectic phase ends, e.g., when the liquid reaches eutectic composition; in the ternary analogue considered here, austenite growth ends when the ferrite approaches uniform composition. In both cases non-equilibrium fractions of the two phases result. At the completion of \( \gamma \) growth in the ternary case the volume fraction of \( \gamma \) is generally greater than the equilibrium volume fraction.

Assuming a uniform manganese concentration in the ferrite at the end of austenite growth allows a mass balance for manganese to be written (cf. 2.23):

\[ \int_{M_f^F}^{M_f^S} (C_2^\gamma [M_f] - C_2^O) \frac{dM_f}{dt} + \int_{M_f^S}^{M_f^F} (C_2^\gamma [M_f] - C_2^O) \frac{dM_f}{dt} = \]

\[ = (1-M_f^F) (C_2^O - C_2^{OF}) \]  

(6.4)
where $M_{f}^{S}$ is the mass fraction of austenite at the end of carbon diffusion controlled growth. For the case of initially homogeneous manganese concentration (with reference to 2.23)

$$\int_{0}^{M_{f}^{S}} C_{2}^{Y} (M_{f}) - C_{2}^{O} dM_{f}^{S} = \int_{0}^{X_{s}} (C_{2}^{Y}(X) - C_{2}^{O}) dX_{o} = 0 \quad (6.5)$$

Combining Eqs. (6.2) and (2.1) gives:

$$C_{2}^{Y}(M_{f}) = a + b \frac{C_{2}^{O}}{M_{f}} \quad (6.6)$$

which is true for $M_{f}^{S} < M_{f} < M_{f}^{F}$. Eqs. (6.5) and (6.6) may be inserted into Eq. (6.4) to recover Eq. (2.26) which indicates that the final volume fraction (for the initially uniform manganese case) is independent of particle shape as well as the scale of the structure.

Eq. (6.6) may be applied whenever Eq. (6.2) holds true, i.e., whenever carbon activity in the austenite and ferrite throughout the material is essentially uniform.

This has been shown to be the case for long times in all cases treated, i.e., cases with particle size differences, initial manganese fluctuations (both over short and long distances). If uniform manganese concentration in the ferrite is assumed (with a frozen manganese profile in the austenite) as the end point for all these cases, then the volume fraction will be determined by Eq. (6.4). All that is required is the estimation of the first integral on the left-hand side of Eq. (6.4), hereafter termed the "$M_{f}^{S}$ integral".
For any homogeneous manganese case (even with particle size differences) the $M_f^S$ integral is zero and Eq. (2.26) gives the final volume fraction. The short wavelength manganese case is easily treated since $C_2^Y[M_f]$ for $M_f < M_f^S$ is the same for all particles due to symmetry conditions.

The case with the limited long wavelength manganese segregation is less easily treated, although upper and lower limits on the final volume fraction may be estimated. Fig. 6.3 illustrates schematically the mass balance considered by Eq. (6.5). Note that Fig. 6.3 a and b are not concentration profiles but graphs of $C_2^Y[M_f]$ vs. $M_f$. The situation depicted in Fig. 6.3a has been discussed and corresponds to an initially uniform manganese distribution, and the $M_f^S$ integral equals zero. Situations where this integral is greater than zero will have smaller volume fractions than the initially uniform manganese case.

Fig. 6.3b shows a situation where the volume fraction associated with full-equilibrium results. This requires:

$$
\int_0^{M_f^E} (C_2^Y - C_2^O) dM_f = M_f^E C_2^{YE}
$$

(6.7)

where $C_2^{YE}$ is the austenite manganese concentration associated with full equilibrium. Eq. (6.7) requires

$$
\int_0^{M_f^S} (C_2^Y - C_2^O) dM_f > C_2^{YE} M_f^S
$$

(6.8)

which requires that, on average:

$$
C_2^Y[M_f] > C_2^{YE} \text{ for } M_f < M_f^S
$$

(6.9)
Eq. (6.9) requires a larger amplitude of the initial manganese fluctuation than would be expected (Kattamis and Flemings, 1965, cf. Section 2.4.3). Smaller amplitudes of the initial manganese fluctuation decrease the $M_f^S$ integral and lead to a final volume fraction greater than the full equilibrium volume fraction.

Fig. 6.3c illustrates the sections of the end point concentration profile to be considered in determining the $M_f^S$ integral for the long wavelength fluctuation. The $M_f^S$ integral will be greater than zero for two reasons:

1. As the finite difference calculations show, (cf. Section 2) austenite particles low on the gradient (where $C_2^D(\gamma) < C_2^O$) are consumed.

2. Particles high on the gradient (where $C_2^D(x) > C_2^O$) experience the greatest amount of growth prior to growth by manganese partitioning and thus make the largest contribution to $M_f^S$.

The end point volume fraction for the case of the long wavelength manganese fluctuation is thus greater than the full equilibrium volume fraction and less than the volume fraction given by Eq. (2.23).

Computed results (for an initial long wavelength manganese fluctuation) indicate that particles high on a manganese gradient grow, taking carbon from particles lower on the manganese gradient. In times of the order of 500 s shrinkage of particles low on the manganese gradient will
commence and particles low on the gradient will be removed in times of the order of $2 \times 10^4$ s (even if capillarity is not considered). As a result intercritical batch annealing might be expected to intensify banding in a steel which exhibits appreciable long range segregation of alloying elements. Such behaviour has been observed experimentally by Speich (1979).

6.2.3 Quaternary Alloys

The quaternary case is similar to the ternary in that the interfacial equilibrium tie-line is expected to change steadily during the period of alloying-element-controlled growth.

Unlike the ternary case, however, the trajectory of the tie-line on the quaternary isotherm is not constrained to lie in any plane but must be determined by a mass balance for carbon combined with the requirement that fluxes of two alloying elements yield the same interface velocity.

One interesting result of the numerical calculations is that in moving from Fe-C-1% Mn to Fe-C-1%Mn-1%Si there is little change in growth rate despite the fact that Si has a diffusion rate ten times greater than Mn. Silicon therefore has mainly a constitutional effect when added to Fe-C-Mn, reducing the volume fraction for a given time in the intercritical anneal. This effect of silicon reflects behaviour in the Fe-C-Si ternary and results from its distribution coefficient being close to 1. The limited effect
of Si is clearly not a general result for quaternary additions. Quaternary additions with distribution coefficients further from 1 would experience a greater amount of partitioning (between ferrite and austenite) and create a larger difference in volume fraction from the ternary.

6.2.4 Cooling Behaviour

Consideration of the behaviour of a binary Fe-C alloy suggests that, upon cooling from the intercritical range, ferrite growth should occur as the interfacial carbon content of austenite increases. The addition of a slow diffusing alloying element leads to the requirement of a finite degree of undercooling before rapid carbon-diffusion-controlled austenite shrinkage can occur. Managanese enrichment of the perimeter of γ particles tends to stabilize that region with respect to ferrite growth; the non-enriched centres become preferred sites for ferrite growth on cooling. The manganese enrichment of the perimeter of the austenite also results in increased "hardenability" in this region. This difference in hardenability may result in a ferrite-pearlite core surrounded by a martensite shell being produced on cooling. Such a structure has been observed by Speich (1980).

It should be noted that hardenability information derived from the behaviour of a bulk material may not easily be applied to regions of similar concentration on a scale of the order of the austenite particle size. Further, some
events usually associated with hardenability, e.g., pro-
eutectoid ferrite nucleation; are clearly inapplicable to
an intercritical anneal. The manganese enriched region of
the austenite has a greater resistance to pearlite formation
and ferrite growth than the non-enriched austenite in common
with the usual concepts of hardenability.

6.3 Suggestions for Further Work and Practical Application

The austenite growth behaviour of ternary Fe-C-Mn
has been characterized for an isothermal anneal followed by
a rapid quench. The major features of the computer modell-
ing have been verified experimentally for the case of an
initially homogeneous manganese distribution. Experimental
verification of the behaviour predicted for more complex
cases (i.e., initially non-homogeneous manganese distribu-
tion and quaternary alloys) would lend further credence to the
theoretical modelling. (A quaternary addition having a more
pronounced effect than silicon would be easier to study ex-
perimentally). Thus far, however, the experimental results
have been shown to be entirely consistent with the principal
assumption used in the modelling studies. The \(\alpha/\gamma\) inter-
faces are, at all times, very close to local equilibrium.

The austenite nucleation behaviour is of central
interest when considering continuously annealing to produce
dual phase steels. Nucleation behaviour may also be of
interest for batch annealed steels if alloying elements are
initially partitioned between ferrite and carbides.
Characterization of the cooling behaviour of the steel is also of importance since austenite shrinkage will determine the volume fraction of martensite in the final structure. The current work outlines theoretically the austenite shrinkage behaviour in a qualitative manner. More quantitative theoretical treatments (i.e., volume fraction predicted as a function of time and cooling rate) are necessary along with further experimental work in this area.
REFERENCES


G.R. Purdy, Int'l Conf. on Solid-Solid Phase Transformations, Pittsburgh, August, 1981.


B. Robertson, private communication, 1981.


Figure 2.1
Initial Condition - A mixture of ferrite and pearlite is heated into the intercritical range to become a mixture of ferrite and austenite whose structure is illustrated schematically in (a). The austenite is initially of eutectoid composition $C_1^E$, with a carbon concentration profile as shown in (b). The manganese concentration is uniform as shown in (c).
Figure 2.2
Carbon Diffusion Controlled Growth - In order to have the same value for interface velocity from both the flux of carbon and the flux of manganese, the manganese gradient in (b) must be $10^4 \times$ steeper than the carbon gradient (a). Associated with the steep manganese gradient is a minute amount of manganese partitioning in the $\gamma$, $C_2^0 = C_2^0$. The tie line associated with the carbon diffusion controlled growth is shown on the isotherm in 2(c).
Figure 2.3
Impingement of carbon diffusion profiles in the $\gamma$ leads to logarithmic carbon diffusion controlled growth. The carbon concentration profile at the end of this stage is shown in fig. 3(b).
Figure 2.4
Growth with Manganese Partitioning: Further $\gamma$ growth occurs by a reduction of $\gamma$ carbon content to $C_1$ below the $C_{1s}$ value as in 4(a). This results in a shift of the tie line from S toward P in 4(c). The tie-line shift corresponds to an increase in $\gamma$ manganese content with the equilibrium interface manganese compositions being "frozen" in the $\gamma$ as in 4b. Associated with this manganese profile is a slight variation in carbon content of the austenite which is necessary for uniform carbon activity. (This variation of carbon content is exaggerated in 4(d)).
Figure 2.5
Calculated rate of austenite growth (volume fraction vs. time) with and without ternary interaction.
Figure 2.6
Managanese concentration profiles for late stages of \( \gamma \) growth. In the late stages of manganese-diffusion-controlled growth, manganese diffusion fields in the ferrite impinge so that all the ferrite becomes depleted in manganese. (a) shows concentration profiles before impingement. (b) shows concentration profiles shortly after impingement and defines \( C_2^I \), the ferrite manganese concentration midway between austenite grains. (c) shows the concentration profile at the end of austenite growth where a slight gradient in the ferrite remains.
Figure 2.7
Concentration profiles for carbon and manganese for different times during the annealing of an Fe-0.08%C-1%Mn alloy at 750°C. Thermodynamic data from Uhrenius (1978): $k_0 = 1.0297$, $k_1 = 0.027$, $k_2 = 0.336$. 
Figure 2.8
Calculated γ growth rate curves (volume fraction vs. log time) for Fe-C-Mn alloys of different composition annealed at 750°C. Volume fractions associated with complete equilibrium (i.e., uniform Mn in γ) are indicated. Thermodynamic data from Uhrenius (1978): $k_0 = 1.0297$, $k_1 = .027$, $k_2 = .336$. 
Figure 2.9
Calculated γ growth rate curves (volume fraction vs. log time) for different ternary alloys annealed at 750°C. Thermodynamic data from Uhrenius (1978): $k_0 = 1.0297$, $k_1 = .027$, $k_{Mn} = .336$, $k_{Si} = 1.3$, $k_{Ni} = .57$. 
Figure 2.10
Calculated concentration profiles. Carbon and manganese concentration profiles for different times for a 1\% Mn alloy assuming a spherical particle, initially 1 micron in radius during isothermal growth at 750\°C.
Figure 2.11
Differences in carbon concentration between particles. A small particle grows more quickly and decreases in carbon concentration faster than a larger particle. Curve A shows the ratio of carbon concentration of large/small particle where initial half widths are 1 and 0.2 μm. Curve B is for half widths of 1 and 0.5 μm. Curve C shows the effect of carbon flux in the ferrite (with initial half widths of 1 and 0.2 μm). A slight difference in carbon concentrations appears only briefly, and a common tie line describes both particles.
Figure 2.12
The common tie line for a system of particles of different sizes is sustained by a constant carbon flux from the large particle to the smaller. As a result the carbon content \((C_{1}^{B}x)\) of the larger particle decreases from its original value, \(C_{1}^{B}x / C_{1}^{E}L_{B}^{E}\), is plotted against time.
Figure 2.13
(a) Initial conditions: A sinusoidal manganese distribution \( C_2^D(X) = A \cos \pi X/W \) has pearlite colonies centred only manganese peaks.
(b) Carbon diffusion controlled growth is accompanied by negligible manganese partitioning \( C_2^I = C_2^D(X_0) \) which combined with Equation (2.1) gives an expression for the locus of interface carbon concentrations shown in (c). A sequence of carbon concentrations are superimposed in (c). Profile 3 in (c) has interface position, \( X_3 \), and uniform carbon concentration, \( C_1^S \).
Figure 2.14
Manganese diffusion controlled growth (for the initial conditions shown in Fig. 2.13a) produces the profile shown in (a) after a short time. The end of growth is associated with the profile shown in (b). The end point volume fraction will equal the full equilibrium volume fraction only for a very large amplitude of the initial manganese fluctuation (as shown in (c)).
Figure 2.15
The distance from $X=0$ to $X=W$ is divided into $K$ grid points for the finite differences calculated. The interface has grid position, $R$. A node from the finite difference grid is shown; the finite difference expression for Fick's second law allows $C_{i}^{t+1}$ to be calculated from $C_{i-1}^{t}$, $C_{i}^{t}$, $C_{i+1}^{t}$.
Figure 2.16
Calculated concentration profiles (manganese concentration vs. distance) for two different methods of computation are shown. The computation as described in Sections 2.1.6 to 2.1.9 gives results very close to the finite difference calculation results.
Figure 2.17
Calculated manganese concentration profiles for a 1000s anneal at 750°C: (b) calculated by finite difference method; (a) calculated using Zener approximation.
Figure 2.18
Carbon diffusion controlled growth in a long manganese gradient.
(a) Initial conditions: austenite of eutectoid carbon concentration
with an initial linear variation of manganese concentration.
(c) Carbon diffusion controlled growth at both sides of the particle
with no manganese partitioning \( C_f = C_2 \cdot X \) leads to a higher inter-
face carbon concentration at the low manganese side of the particle
(as determined by the ternary isotherm (b)). Growth at the left side
of the particle ceases when there is no longer a flux of carbon toward
the interface (d). Carbon flux away from the interface at the left,
reduces the interface carbon concentration (e). The manganese in-
terface concentrations adjust to maintain local equilibrium. Growth of
the particle is complete at (f) with a common tie line describing both
interfaces.
Figure 2.19
Rapid interface motion (by carbon diffusion method) must be accompanied by a very steep manganese gradient. A mass balance indicates that negligible manganese partitioning must accompany such rapid interface motion. The manganese concentration profile in (a) is consistent with rapid austenite growth: $C_2^\gamma = C_2^\alpha(X)$. The manganese concentration profile in (b) is consistent with rapid austenite shrinkage: $C_2^\gamma = C_2^\gamma(X)$. The manganese concentration profile in (c) cannot move quickly and will result in austenite growth controlled by diffusion of manganese in ferrite (since $D_2^{\alpha} >> D_2^{\gamma}$).
Figure 2.20
Carbon diffuses in the ferrite between particles on a long manganese gradient. The initial condition (before transfer of carbon between particles) is shown in (a) and is similar to that in Fig. 2.18(c). Carbon flux from the particle low on the gradient to the particle higher on the gradient results in motion of the interface at $Y_0$, as in (b). The carbon flux will end when a common tie-line describes all interfaces, as in (c).
Figure 2.21
The initial condition for manganese diffusion controlled growth of three austenite particles on a long manganese gradient is shown. A common tie-line describes all six interfaces. Some variables associated with the finite difference calculation are defined.
Figure 2.22
Calculated concentration profiles. Manganese concentration vs.
distance is shown for different times for growth of austenite in a
long manganese gradient. Insets to the right of each particle show
the detail of the concentration profile. The full vertical scale is
3 wt.% Mn in both large graphs and insets. The full horizontal scale
is 100 μm for the large graphs and 5 μm for the insets.
Figure 2.23
Calculated concentration profiles. Manganese concentration vs. distance is shown for different times for growth of austenite in a long manganese gradient. Insets to the right of each particle show the detail of the concentration profile. The full vertical scale is 3 wt.% Mn in both large graphs and insets. The full horizontal scale is 100 μm for the large graphs and 5 μm for the insets.
Figure 3.1
The quaternary isotherm (a) is a tetrahedron where the α/α + γ and γ/α + γ boundaries are surfaces. These surfaces are connected by tie lines so that specifying two interface concentrations fixes all other interface concentrations (cf. Equation 3.1). The initial growth stage in the quaternary case is carbon-diffusion-controlled. The finite gradient in the carbon concentration profile (b) is accompanied by very steep gradients in the manganese and silicon concentration profiles: (c) and (d), respectively. A mass balance associates only a minute amount of partitioning with the carbon-diffusion-controlled growth: $C_2^Y \sim C_2^0$, $C_3^Y \sim C_3^0$. 
Figure 3.2
Concentration profiles for Si (a) and Mn (b) during growth with alloying-element-control. Fluxes of both Si and Mn are used to determine separate expressions for interface velocity for a given interface position. $C_1^y(X)$ and $C_2^y(X)$ are determined iteratively for incements of interface position such that both velocities are equal.
Figure 3.3
Concentration profiles for carbon and manganese for different times during the annealing of an Fe-0.08%C-1%Mn-1%Si alloy at 750°C. Same thermodynamic data as Figure 2.3 with $k_3 = 1.3$. 

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Figure 3.4
Calculated γ growth rate curves (volume fraction vs. log time) for Fe-.08%C-1%Mn and Fe-.08%C-1%Mn-1%Si alloys annealed at 750°C. Data is the same as for Figures 2.9 and 3.3.
Figure 4.1
After a short isothermal anneal at temperature, $T_S$, where $\gamma$ growth has occurred with no appreciable manganese partitioning, tie line $S$ in (a) describes the interface concentrations. Carbon diffusion controlled austenite shrinkage occurs at temperatures below $T_B$, e.g., $T_C$ where tie line $C$ may be drawn. Tie line $C$ has $C^{sc}_2 = C^c_2$ so that no manganese is partitioned upon shrinkage as shown in the manganese concentration profile, (b). Also, $C^{sc}_1 > C^c_1$ as in the carbon concentration profile, (c).
Figure 4.2
A small amount of cooling after isothermal growth with no manganese partitioning. Tie line $S$ in (a) describes the interface compositions after a short isothermal anneal at temperature, $T_s$. Cooling to a temperature above $T_b$, e.g., $T_a$ results in continued growth with manganese partitioning. Tie line "a" in (a) describes the interface compositions. The concentration profiles for manganese and carbon are shown in (b) and (c), respectively. The slow rate of growth associated with manganese partitioning requires a very flat gradient in carbon concentration, $C_1^c = C_1^s$. 
Figure 4.3
After a short isothermal anneal at temperature, $T_s$, where $\gamma$ growth has occurred with no appreciable manganese partitioning, the line with arrows indicates the trajectory of $\gamma$ interface compositions produced upon continuous cooling. This trajectory is the locus described by the $\gamma$ end of tie lines upon cooling. Above temperature, $T_b$, manganese diffusion controlled $\gamma$ growth occurs and below $T_b$ carbon diffusion controlled austenite shrinkage occurs.
Figure 4.4
During a long isothermal anneal at $T_S$ the tie line describing the interface compositions shifts from s to t producing a manganese concentration profile similar to that shown in Fig.2.4b. For carbon diffusion controlled $\gamma$ shrinkage to occur at the original $\alpha/\gamma$ interface, the material must be cooled below $T_g$, e.g., $T_g^\prime$. In this range of temperature the line gg' may be drawn which fulfills two criteria: $C_2^{g^\prime} = C_2^t$, as shown in (b) and $C_1^{g^\prime} > C_1^t$, as in (c).
Figure 4.5
When the material is annealed as described for Fig. 4.4, cooling to temperatures above $T_e$, e.g., $T_d$ causes continued $\gamma$ growth with manganese partitioning controlled by manganese diffusion. The associated slow growth rate requires a flat carbon concentration profile as in (c), i.e., $C_{\gamma}^d = C_{\gamma}^i$, thus defining tie line d in (a). In this temperature range ($T_s$ to $T_o$), $C_{\gamma}^d < C_{\gamma}^i$. 
When the material is annealed as described for Fig. 4.4, cooling to temperatures between $T_e$ and $T_g$, e.g., $T_f$ produce a complex situation. At the original $\alpha/\gamma$ interface $\gamma$ shrinkage occurs controlled by diffusion of manganese both in $\alpha$ and in $\gamma$. The associated carbon gradient is very flat (as in (c)) which gives $C_f^\gamma = C_e^\gamma$. This defines tie line $f$ in (a). In this temperature range the lines such as $f$ have $C_f^{2\gamma} > C_f^\gamma$. When shrinkage moves the interface to position $x_f$ in (b), then shrinkage may continue with no manganese partitioning, i.e., by carbon diffusion control. At any temperature below $T_e$ carbon diffusion controlled $\gamma$ shrinkage is possible in the centre of the $\gamma$ where it is not enriched in manganese.
Figure 5.1
Quantimet Data. Observed volume fraction is plotted against annealing time and compared with predicted volume fraction vs. time curves. Curve U is constructed using the thermodynamic data of Uhrenius (1978): $k_0 = 1.0297$, $k_1 = 0.027$, $k_2 = 0.336$. Curves PP and PS use the thermodynamic data of Gilmour et al. (1972): $k_0 = 1.0339$, $k_1 = 0.026$, $k_2 = 0.407$. Curves are for spherical kinetics with ($L = 1.6 \text{um}$) except for PP which is for planar kinetics. The length P.O. is the typical perimeter output of the Quantimet expressed as an area fraction (by assuming the interface is one picture point, 0.42 $\text{um}$, wide). The results are for experimental steel A: Fe-0.056%C-0.97%Mn.
Figure 5.2
Quantimet Data. Observed volume fraction is plotted against annealing time and compared with predicted volume fraction vs. time curves. Curve U is constructed using the thermodynamic data of Uhrenius (1978): $k_0 = 1.0297$, $k_1 = 0.027$, $k_2 = 0.536$. Curves PP and PS use the thermodynamic data of Gilmour et al. (1972): $k_0 = 1.0339$, $k_1 = 0.026$, $k_2 = 0.407$. Curves are for spherical kinetics with ($L = 1.6$ μm) except for PP which is for planar kinetics. The length P.O. is the typical perimeter output of the Quantimet expressed as an area fraction (by assuming the interface is one picture point, 0.42 μm, wide). The results are for experimental steel B: Fe-0.079%C-0.99%Mn.
Figure 5.3
Quantimet Data. Observed volume fraction is plotted against annealing time and compared with predicted volume fraction vs. time curves. Curve U is constructed using the thermodynamic data of Uhrenius (1978): \( k_0 = 1.0297, k_1 = 0.027, k_2 = 0.336 \). Curves PP and PS use the thermodynamic data of Gilmour et al. (1972): \( k_0 = 1.0339, k_1 = 0.026, k_2 = 0.407 \). Curves are for spherical kinetics with \( l = 1.6 \mu m \) except for PP which is for planar kinetics. The length P.O. is the typical perimeter output of the Quantimet expressed as an area fraction (by assuming the interface is one picture point, 0.42 \( \mu m \) wide). The results are for experimental steel C: Fe-0.50%C-0.97%Mn.
Fig. 5.4
Electron microprobe measurements were taken from the specimen in the as-polished condition (b). In order to scan through the centre of a large martensite particle (and avoid sectioning effects), the specimen was first etched and marked with a microhardness indenter (c) following after microprobe analysis made determination of the probe indenter position possible using the contamination limit (d). Superimposing the negatives of (c) and (e) produced (d) which indicates that the particle indicated by the arrow in (c) was scanned in order to produce the concentration profile in Fig. 5.6.
Figure 5.5
Convoluted concentration profiles and the effects of metallographic sectioning. Sectioning closer to the particle edge increases the strength of the microprobe signal, although resolution of the non-enriched region in the particle centre is lost.
Figure 5.6
A predicted concentration profile is included with an expected microprobe trace (i.e., the convolution of the predicted profile) and compared with experimental points. The specimen is an Fe-0.08%C-1%Mn alloy annealed 50 h at 750°C. The particle scanned is shown in Fig. 5.4.
Figure 5.7
A predicted concentration profile is included with an expected microprobe trace (i.e., convolution of the predicted profile) and compared with experimental points. The specimen is an Fe-0.08%C-1%Mn alloy annealed 6 days at 800°C. The apparent lack of a non-enriched region in the particle centre may be explained by the sectioning effects shown in Fig. 5.5.
Figure 5.8
Schematic diagram of x-ray detection geometry in McMaster HB5 STEM.
Figure 5.9
Peak broadening due to sectioning effects. A concentration profile along XX' in (a) is shown in (d) and has a peak width, W. If the interface is inclined to the beam by an angle, then peak broadening will occur even for an infinitesimal probe as in (a) where the apparent peak width will increase to PP': PP' = W/cos φ + t tan φ. Approximating the probe to a cone of semi-angle γ leads to an apparent peak width of QQ': QQ' = t(tan φ + tan γ) + W/cos φ + S for γ < φ. The apparent peak width is RR': RR' = W/cos φ + 2 t tan φ + S. S is spot size and t is foil thickness for φ < φ.
Figure 5.10
Reduction in the height of concentration peaks due to sectioning effects. The observed concentration for a given probe position is related to the range of compositions sampled by the probe. The range of concentrations is determined by the projection, P, of the probe on XX' (a line normal to the iso-concentration planes). For the infinitesimal probe in (a), P is given by: \( P = t \sin \phi \). For the conical probe considered in (b) and (c), P is given by:
\[
P = (s + t \tan \theta + t \tan \phi) \cos \phi \quad \text{when} \quad \phi > \theta \quad \text{and}
\]
\[
P = (s' + 2t \tan \theta) \cos \phi.
\]
If x-rays are generated with uniform intensity throughout the concentration range sampled the observed peak height for the profile in (d) will be \( C_2' \) where \( C_2' = C_2 + \frac{m}{2P} \) and \( m \) is the slope of the concentration profile.
Figure 5.11
Schematic of typical x-ray spectrum (counts vs. energy). Shaded regions were used in a linear regression of normalized background per channel. Normalized background per channel for window 1 is given by: $W1/((W1 + W2 + W3 + W4) \times \text{Channel Width})$ where $W1$ is the total number of counts in the window indicated.
Figure 5.12
Effect of absorption in background shape. B1 and B4 are the total numbers of counts in the windows shown in Figure 5.11. The total FeKα counts in 100's is related to the specimen thickness as is the amount of absorption. If absorption is affecting the background shape through the range of thicknesses encountered, B1/B4 should decrease at high count rates.
Figure 5.13
An observed concentration profile is shown along with a predicted profile. The observed concentrations are the net \( \text{MnK}^\alpha / \text{FeK}^\alpha \) ratios without standardization. The sample is an Fe-0.08\%C-1\%Mn steel annealed 500 s at 750\(^\circ\)C.
Figure 5.14
Cambridge HB5 STEM results. An observed manganese concentration profile is shown along with a predicted profile. The concentration profile is that of Fig. 5.13 standardized by shifting all concentration downward by 0.2% (using the concentrations far from the interface as an internal standard). The sample is an Fe-0.08%C-1%Mn steel annealed for 500s at 730°C.
Figure 5.15
Phillips 400 TEM/STEM results. An observed manganese concentration profile is shown along with a predicted profile. The sample is an Fe-0.08%C-1%Mn steel annealed for 500 seconds at 750°C. Concentrations plotted are the net Mn$k\alpha$/Fe$k\alpha$ intensity ratio without alteration.
Figure 5.16
Cambridge HB5 STEM results. An observed manganese concentration profile is shown along with a predicted profile. The same is an Fe-0.08%C-1%Mn steel annealed for 100 seconds at 750°C. The concentrations have been standardized as for Fig. 5.14.
Figure 5.17
McMaster HBS STEM results. A predicted manganese concentration profile is shown along with an observed concentration profile. Concentrations plotted are the net MnKα/FeKα intensity ratio without alteration. Different sets of points result when different data is used in the linear regression program for background. Round points use background data only from the 19 spectra associated with the points in this profile. Points marked with Δ use 55 spectra as input for the background calculation (i.e., other McMaster HBS spectra associated with the data points in 5.18). The specimen is an Fe-0.08% C-1%Mn steel annealed 100s at 750°C.
Figure 5.19
A micrograph of a 1% Mn steel, annealed for 6 days at 800°C (x1000) slow cooled for 6 seconds, then water quenched. Note that many of the austenite (martensite) particles have ferrite cores. This is attributed to the "locking" of the original α/γ interfaces by the manganese profiles developed during isothermal growth.
Figure 6.1
Calculation γ growth rate curves (volume fraction vs. log time) compared with observed growth rate curves from Speich (1981) for Fe-C-Mn steel annealed at 740°C. Volume fractions associated with complete equilibrium (i.e., uniform Mn in γ) are indicated. Thermodynamic data from Gilmour et al. (1972a): $k_0 = 1.0339$, $k_1 = 0.026$, $k_2 = 0.407$. 
An analogy may be drawn between γ growth controlled by alloying element diffusion and classical non-equilibrium freezing. If the ternary isotherm, (a), is drawn with chemical potential of carbon substituted for carbon concentration, (b), then carbon chemical potential becomes analogous to temperature in the freezing case, (c). In both cases a locus of equilibrium concentrations is left behind by the advancing interface with this equilibrium concentration being related to the fraction transformed by a mass balance.
Figure 6.3
Manganese concentration as a function of mass fraction is shown in (a) and (b) for the end of austenite growth. (a) is associated with an initially homogeneous manganese distribution where the final mass fraction of austenite, \( M_f \), is given by (2.26). (b) is associated with the full equilibrium volume fraction, \( M^{eq}_f \), and requires a very large amplitude of the initial manganese fluctuation. The end point concentration profile for a long wavelength manganese fluctuation, shown in (c), will have a final mass fraction between \( M^{eq}_f \) and \( M_f \). Sections of the profile in (c) marked with a * contribute to the \( M^{eq}_f \) integral.
Figure A.1
Schematic illustration of manganese concentration profile used to solve the mass balance for manganese in Appendix III. Step-wise integration of:

\[ \int_{X_2}^{X_0} (C_x - C_0) \, dx \]

gives \( M_6 = M_4 + (M_4 - M_0) X_1 \) where \( M_4 \) is the previous value of \( M_6 \).
APPENDIX I

EXPLANATION OF NOTATION

An attempt was made to be consistent in notation.

The following system applies except where variables are defined otherwise (Section 2.6.4 is an exception).

**Variables**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2, B_1$</td>
<td>Defining an initial Mn gradient</td>
</tr>
<tr>
<td>$a, b, c$</td>
<td>These variables define local equilibrium relations between interface concentrations (given in (2.1) and (3.1)).</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>$J$</td>
<td>Flux</td>
</tr>
<tr>
<td>$k$</td>
<td>Distribution coefficient</td>
</tr>
<tr>
<td>$L$</td>
<td>Original particle half width (or radius)</td>
</tr>
<tr>
<td>$M_f$</td>
<td>Mass fraction of austenite</td>
</tr>
<tr>
<td>$R$</td>
<td>Ratio of off-diagonal to on-diagonal diffusion coefficients</td>
</tr>
<tr>
<td>$r$</td>
<td>Distance from centre of symmetry (for a spherical geometry)</td>
</tr>
<tr>
<td>$T$</td>
<td>Total carbon content of an austenite particle</td>
</tr>
<tr>
<td>$X$</td>
<td>Distance (from centre of symmetry) for a planar geometry</td>
</tr>
<tr>
<td>$W$</td>
<td>Width of smallest symmetry unit</td>
</tr>
</tbody>
</table>
Subscripts and Superscripts

Numerical

C, D, J and k invariably have a numerical subscript: 1 indicates carbon, 2 indicates manganese, 3 indicates silicon. \( k_o \) is the distribution coefficient for Fe. C with a superscript 0 (or o) indicates bulk concentration. \( C_1 \) indicates austenite carbon concentration. Numerical subscripts on \( r \) are defined in the text.

Greek

Greek letters never appear as subscripts. \( \alpha \) means ferrite, \( \gamma \) indicates austenite. C with a superscript that is either a Greek letter alone or a Greek letter with a lower case Roman letter refers to an interface concentration, e.g., \( C_2^{\alpha} \) or \( C_2^\gamma \). A small Roman letter associates the interface concentration with a particular tie-line.

The exception to this is expressions such as \( C_2^\gamma[X] \) which refers to manganese concentration varying as a function of distance in the austenite.

Roman

Roman subscripts and superscripts have the following meanings:
Subscript or Superscript | The subscript or superscript variable is associated with:
--- | ---
A | Large austenite particle
B | Small austenite particle
E | Full equilibrium volume fraction
F | The end of austenite growth
I | The position of impingement
L | An austenite particle low on a manganese gradient
R | An austenite particle high on a manganese gradient
$\xi$ | The end of carbon diffusion controlled growth

$C^D_2(X)$ indicates initial manganese concentration as a function of distance. $X_0$ indicates interface position.
APPENDIX II

AUSTENITE GROWTH CALCULATION FOR
TERNARY Fe-C-Mn, PLANAR GEOMETRY

The following program calculates the growth rate of austenite for an isothermal anneal of ternary Fe-C-Mn with planar geometry according to the model presented in Section 2.1. Only the growth rate during the manganese partitioning stage is calculated. The effect of ternary interaction is neglected (cf. Section 2.1 (f)) while the effect of diffusion of Mn in the γ is included (cf. Section 2.1(a)).

In the program $C_1$ is used as the independent variable and is decreased step-wise by the amount $D3$. Eq. (15) associates an interface position $\chi \theta$ and a change in interface position $\chi 3$ with each value of $C_1$. Eqs. (13), (20) and (21) enable the components of interface velocity $G(=\frac{dx_0}{dt})$ to be calculated.

The time increment associated with the change in interface position is given by:

$$\Delta t = \int_{\chi 5}^{\chi \theta} \frac{1}{G} \, d\chi$$

where $\chi 5$ is the previous interface position. This integral is evaluated using the trapezoidal rule in the program to determine the total time, $T$.

The following table indicates the correspondence between program variables and variables in the text (where applicable).
<table>
<thead>
<tr>
<th>Program</th>
<th>Text</th>
</tr>
</thead>
<tbody>
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<td>CØ</td>
<td>$C^E_1$</td>
</tr>
<tr>
<td>C2</td>
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</tr>
<tr>
<td>D2</td>
<td>$D^\gamma_2$</td>
</tr>
<tr>
<td>D4</td>
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<td>$C^\gamma_2$</td>
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<tr>
<td>C4</td>
<td>$C^\alpha_2$</td>
</tr>
<tr>
<td>C5</td>
<td>$C^{\alpha I}_2$</td>
</tr>
</tbody>
</table>
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COPIE DE QUALITEE
APPENDIX III

CALCULATION OF AUSTENITE GROWTH FOR NEIGHBOURING PARTICLES OF DIFFERENT SIZES

The following table indicates the correspondence between variables and expressions in the text and variables in the computer program.

<table>
<thead>
<tr>
<th>Program</th>
<th>Text</th>
<th>Program</th>
<th>Text</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>$C^O_1$</td>
<td>FY</td>
<td>$C^A_1 Y_0$</td>
</tr>
<tr>
<td>L</td>
<td>$L^B$</td>
<td>FP</td>
<td>$C^E_1 L^A$</td>
</tr>
<tr>
<td>L2</td>
<td>$L^A$</td>
<td>J1</td>
<td>$J_1^\alpha$</td>
</tr>
<tr>
<td>EØ, MØ</td>
<td>$C^O_2$</td>
<td>B</td>
<td>$b$</td>
</tr>
<tr>
<td>D2</td>
<td>$D^\alpha_2$</td>
<td>A</td>
<td>$a$</td>
</tr>
<tr>
<td>D1</td>
<td>$D^\alpha_1$</td>
<td>G</td>
<td>$2W$</td>
</tr>
<tr>
<td>CØ</td>
<td>$C^E_1$</td>
<td>E6, M6</td>
<td>$\int_{x_s}^{x_0} (C^O_2 - C^O_2) dx$</td>
</tr>
<tr>
<td>CX</td>
<td>$C^B_1 X_0$</td>
<td>E1, M1</td>
<td>$C^\gamma_2$</td>
</tr>
<tr>
<td>CP</td>
<td>$C^E_1 L^B$</td>
<td>E2, M2</td>
<td>$C^\alpha_2$</td>
</tr>
</tbody>
</table>

Additional variables are described in REM statements in the program. Figure A1 illustrates schematically the manganese concentration profile used to determine the bulk mass balance for manganese and subsequently the interface velocity. $M_6$ is given by:

$$M_6 = M_4 + (M_1 - M_0) \times 1$$

where $M_4$ is the previous value of $M_6$, i.e., before the time increment, $T_1$. 
110 REM INITIAL VELOCITY FOR THE LARGER
111 U = UH + UH - UL
112 V = VH
113 W = WH
114 REM THE INCREMENT OF INTERFACE
115 REM POSITION FOR THE SMALLER
116 REM PARTICLE YL MUST BE CHANGED
117 REM SUCH THAT THE TIME INCREMENT
118 REM WHICH RESULTS IN THE SAME W
119 REM HAS CALCULATED FOR THE LARGER
120 REM PARTICLE. THE LOOP WHICH
121 REM FOLLOWS IS A NEWTON-RAPHSON
122 REM ITS ITERATION WHICH MAKES THIS SO.
123 FOR I = 1 TO 10
124 YH = YH + YI
125 E1 = EY + YH
126 E1 = E + E + E1
127 E1 = E1 + E1
128 U = U + YH
129 U = UM + YH - UM + YH
130 L = YH - YH
131 EP = -E + EY + YH
132 X = X + X
133 PX = PX + U + PX + U + PX + U + PX + U
134 YH = YH + E1 + YH + E1
135 E1 = E1 - E1 + E1 + E + E1 + E
136 E1 = E1 + U + E1 + E1 + E1 + E1 + E1 + E1
137 E1 = E1 + E1 + E1 + E1 + E1 + E1 + E1 + E1
138 E1 = E1 + E1 + E1 + E1 + E1 + E1 + E1 + E1
139 E1 = E1 + E1 + E1 + E1 + E1 + E1 + E1 + E1
140 EXIT IF = "STOP" : EXIT
141 EXIT IF = "STOP" : EXIT
142 EXIT IF = "STOP" : EXIT
143 EXIT IF = "STOP" : EXIT
144 REM REM
APPENDIX IV

FINITE DIFFERENCE CALCULATION
FOR THE GROWTH OF A SINGLE AUSTENITE PARTICLE

The Murray-Landis variable grid is used where a grid point is always a constant fraction of the instantaneous phase thickness. Thus the spatial position, \( X_I \), associated with grid point \( I \) is given by:

\[
X_I = \frac{I}{R} X_0 \quad \text{(in austenite)} \quad \text{(A4.1a)}
\]

and

\[
X_I = \frac{I}{K} \frac{R}{R} (W - X_o) + X_o \quad \text{(in ferrite)} \quad \text{(A4.1b)}
\]

As a result the spatial position of each grid point moves as the interface moves. The differential of (A4.1) relates \( \frac{dX_I}{dt} \) to the interface velocity \( \frac{dx_o}{dt} \).

Interface velocity (\( V_l \) in the program) is again given by Equations (19) to (21). However, now the fluxes at the interface are derived by using finite difference formulae for the concentration gradients in Fick's first law.

The concentration change at each grid point (other than the interface) is then given by:

\[
\frac{dC_I}{dt} = \frac{\partial C_I}{\partial X_I} \left( \frac{dX_I}{dt} \right) + \frac{\partial C_I}{\partial t} \quad \text{(A4.2)}
\]

Fick's second law (via a finite difference approximation of \( \frac{\partial^2 C}{\partial X^2} \) gives:

\[
\frac{\partial C_I}{\partial t} = F_2 \left( C_{I-1} - 2C_I + C_{I+1} \right) \quad \text{(A4.3)}
\]
where \[ F_2 = D_2 \left( \frac{R-2}{X} \right)^2 \] (in austenite)

and \[ F_2 = D_2 \left( \frac{K-R}{G-X} \right) \] (in ferrite)

The finite difference approximation for \[ \frac{\partial C_I}{\partial X_I} \] is:

\[ (C_{I+2} - C_{I-1}) / 2\Delta X \] \hspace{1cm} (A4.4)

where \[ \Delta X = X_0 / (R-2) \] (for austenite)

and \[ \Delta X = (G-X_0) / (K-R) \] (for ferrite)

Equations (A4.3) and (A4.4) with the differential of (A4.1) may be inserted in (A4.2) to give \( \frac{dC_I}{dt} \). Expressing \( \frac{dC_I}{dt} \) in forward differing form relates the concentration at time, \( t \), \( C_I^t \) to the concentration at time, \( t+\Delta t \), \( C_I^{t+\Delta t} \):

\[ \frac{dC_I}{dt} = \frac{C_I^{t+\Delta t} - C_I^t}{\Delta t} \] \hspace{1cm} (A4.5)

Equation (A4.5) is rearranged to give lines 3350 and 3430 in the computer program which follows.

The time increment, \( T_1 \), increases and never exceeds 0.01T where T is the total time. Instabilities in the finite difference solution may develop if this time increment is too large. A condition sufficient for preventing this is:

\[ T_1 \leq 0.2 / F_2 \]

(Tanzilli and Heckel, 1968)

To prevent too large a time increment while shortening program running time the spatial grid is coarsened (decreasing \( F_2 \)) by program lines 3550 to just below 3570. A maximum
grid coarseness is also set which prevents grid coarsening (below 30 grid points in the ferrite) and time increment increases.

Most program variables may be identified by the table in Appendix II. Other variable names and exceptions are given below or noted in the program listing.

<table>
<thead>
<tr>
<th>Program</th>
<th>Text</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR</td>
<td>R</td>
</tr>
<tr>
<td>G</td>
<td>R</td>
</tr>
<tr>
<td>F2G</td>
<td>F2 in austenite</td>
</tr>
<tr>
<td>F2A</td>
<td>F2 in ferrite</td>
</tr>
<tr>
<td>C(I,1)</td>
<td>$C^t_I$</td>
</tr>
<tr>
<td>C(I,2)</td>
<td>$C^{t+1}_I$</td>
</tr>
</tbody>
</table>

The program could be altered to treat the case described in Section 2.4 by solving for $X7$ using Eq. (2.37), then altering the initial manganese profile (program lines 3170 to 3210).
THE FILE NAME MEANS FINITE DIFFERENCE UNIFORM MANGANESE

EDIT DIMENSION LINE TO BE CONSISTENT WITH K!

DIMENSION C(500,2)
LOGICAL*: STRING(133), STAB(100)
SCAL(ZMIN, ZMAX, MAXZ, K)=ZMIN+FLOAT(K-1)*(ZMAX-ZMIN)/FLOAT(MAX)
REAL K0, K1, K2, M0, L
OPEN UNIT=6, FILENAME='DK:FDSP.OUT', ERR=8000
CALL SCOPY(' '*1234 + 3 4 5 6 7 8 9 '+', STAB)
MAX=LEN(STAB)
100 FORMAT(F11.2, F9.3, E12.3, 4F9.4, F6.1, 2E12.3)
101 FORMAT(' TI REDUCED ')
102 FORMAT(8X, 'TIME X0', 8X, 'VEL C2-GAMMA C2-ALPHA C1', 5X
2 VOL FRAC T1 V1A V1G ')
103 FORMAT(' T1 = ', F9.3)
104 FORMAT(' K = ', I8, ', IR = ', I8, ', F2A = ', E12.3)
105 FORMAT(12X, '(MICRONS) CM/S (PERCENT)')
120 FORMAT(' KFLAG TRIGGERED')
110 FORMAT(' KOLD THEN KNEW ARE', 2I8, ', F2A = ', E11.3, ', T1 = ', E11.4)
121 FORMAT(' CMEAN = ', F10.4)
111 FORMAT(' GRID COARSENING IS BEING UNDERTAKEN', I8)
2 B X = ', E9.2)
222 FORMAT(' V1A FOLLOWED BY V2A ARE ', 2E11.2)
300 FORMAT(6F11.4)
301 FORMAT(3E12.4)
302 FORMAT(6F11.4)
303 FORMAT(' FLUXVX = ', E11.2, ', FLUXXY = ', E11.2)
304 FORMAT(' OK ')
305 FORMAT(' KS ARE ', 3F9.4)
306 FORMAT(F9.6, 19)
307 FORMAT(' TIME THEN TI ARE ', 2F15.2)
308 FORMAT(2I8)
309 FORMAT(' 0 OUTPUT OK AVERAGE CONC = ', F8.5)
310 FORMAT(F12.2, F9.4)
311 FORMAT(' INPUT/OUTPUT ERROR ENCOUNTERED ')
333 FORMAT(' 0 PROGRAM PROPERLY TERMINATED ')
501 FORMAT(' PROGRAM FINISHED ')
FGRID=8
KFLAG=1
T2=1
TPLLOT=10
TFC=TP
1000 K=2000
1010 T=0
1020 T10=1
2000 J=K+1
3000 D4=1 0E-14
3010 D2=2 0E-12
3020 T1=1
3030 K0=1 0297
3040 K1=0 027
3050 K2=0 336
3060 C0=0 0325 EUTECTOID CARBON AT%
3070 CB=0 0327 BULK CARBON
3080 M0=0 0101 BULK MANGANESE
3090 L=0 0001 Austenite Half Width
3100 G=C0*L/CB! Grain Half Width
3110 A=(K0=1.0)/(K0-K2)
3120 B=(K1-K0)/(K0-K2)
3130 C7=(M0-A)/B
3140 X7=C0*L/C7
3150 IR=INT(K*X7/C)
3170 DO 3200 I=1,K
3200 C(I,1)=M0
3210 C3=M0
3220 C4=K2*M0
3230 X0=X7
3240 F2A=D2*(K-IR)*(K-IR)/((G-X0)*(G-X0))
3250 WRITE(7,104)K,IR,F2A
3260 WRITE(6,104)K,IR,F2A
3270 WRITE(7,102)
3280 WRITE(6,102)
3290 WRITE(6,105)
3300 DO 3601 I=2,K
3325 DO 3599 I=1,1000
3340 C1=C0*L/X0
3240 C3=A+B*C1
3244 C4=K2*C3
3250 C(J,1)=G(K,1)
3260 C(I,1)=C2,1
3270 C(IR,1)=C3
3280 V1A=D2*(K-IR)*(4*C(IR+1,1)-3*C4-C(IR+2,1))/(2*(G-X0)*(C3-C4))
3290 V1C=D4*(IR-2)*(3*C3-4*C(IR-1,1)+C(IR-2,1))/(2*X0*(C3-C4))
3300 V1A=(V1A-V1C)
3310 F2G=D4*(IR-2)*(IR-2)/(X0*X0)
3330 DO 3500 I=2,IR-1
3340 C(I,2)=(I-2)*(C(I+1,1)-C(I-1,1))*V1/2/X0+F2G*
3350 2*(C(I-1,1)-2*C(I,1)+C(I+1,1)))*T1+C(I,1)
3440 C(IR,1)=C4
3460 DO 3430 I=IR+1,K
3470 F2A=D2*(K-IR)*(K-IR)/((G-X0)*(G-X0))
3480 C(I,2)=(K-1)*(C(I+1,1)-C(I-1,1))*V1/(2*(G-X0))*F2A*
3490 2*(C(I-1,1)-2*C(I,1)+C(I+1,1)))*T1+C(I,1)
3500 V2=(D2*(K-IR)*(4*C(IR+1,2)-3*C4-C(IR+2,2))/(2*(G-X0))-D9*(IR
\[ 2\times (3C_3 - 4C_1 + 2C_{IR-1,2} + C_{IR-2,1})/(2\times X_0) / (C_3-C_4) \]

3450 DO 3460 I=2, K
3460 C(I,1) = C(I,2)
3470 T = T - T1
3475 X0 = X0 + T1 * V1
       VOLF = 100 * CB/C1
       IF (V1 LT. -0.1E-9) GOTO 8009
       IF (T .GT. TP) GOTO 3480
       GOTO 3493
3480 C3PCT = 100 * C3
       C1PCT = 100 * C1
       C4PCT = 100 * C4
       XOMIC = 10000 * X0
       WRITE (6, 100) T, XOMIC, V1, C3PCT, C4PCT, C1PCT, VOLF, T1, VIA, V1G
       WRITE (7, 100) T, XOMIC, V1, C3PCT, C4PCT, C1PCT, VOLF, T1, VIA, V1G
       IF (X0 LE. 0.0) GOTO 3600
       TP = TP + TPC
       IF (T .GE. 100000.) GOTO 3599
       IF (T .GE. TPLOT) GOTO 3600
       IF (T .GE. (10 * TPC)) GOTO 3492
3485 GOTO 3493
3492 TPC = 10.0 * TPC
       GOTO 3599
3493 T10 = T1
       FT = 0.1
       IF (KFLAG .EQ. 0) GOTO 3599
       IF (T1 LE. (FT*T)) T1 = FT*T
       IF (T1 GE. (0.2/F2A)) GOTO 3550
       GOTO 3559
       F2A = D2*(K-IR) / ((G-XO)*(G-X0))
3550 KOLD = X
       KNEW = INT(FGRID*(K-IR)) + IR
       IF ((KNEW-IR) .LT. 30) GOTO 3555
       GOTO 3560
3555 KNEW = IR + 30
       KFLAG = 0
       FGRID = 30. / (KOLD-IR)
3560 FGRID = FLOAT(KNEW-IR) / (K-IR)
       DO 3570 I = IR, KNEW
       REI = (I-IR) / FGRID + IR
       IO = INT(REI)
3570 C(I,1) = C(IO,2) + (REI-IO)*(C(IO+1,2) - C(IO,2))
       K = KNEW
       J = K + 1
       F2A = D2*(K-IR) / ((G-XO)*(G-X0))
       IF (KFLAG .EQ. 0) T1 = 0.2/F2A
       WRITE (7, 111) IR
       WRITE (6, 111) IR
       WRITE (6, 100) T, XOMIC, V1, C3PCT, C4PCT, C1PCT, VOLF, T1
       WRITE (7, 100) T, XOMIC, V1, C3PCT, C4PCT, C1PCT, VOLF, T1
WRITE (6,110) KOLD, KNEW, T2A, T1
WRITE (7,110) KOLD, KNEW, T2A, T1
IF (T1 <= 0.21/T2A) GOTO 3550
GOTO 3599
C
C
3600 WRITE (7,103) T1
IF (T GT 1000000) GOTO 4060
IF (T GT 100000) GOTO 4050
IF (T.GT.10000.) GOTO 4040
IF (T.GT.1000.) GOTO 4035
IF (T.GT.100.) GOTO 4030
IF (T.GT.10.) GOTO 4020
IF (T.GT.1.) GOTO 4010
OPEN (UNIT=8, NAME= 'DK:FE0.IO', TYPE= 'NEW', ERR=8000,
2ACCESS= 'SEQUENTIAL', FORM= 'FORMATTED')
TPLOT=10 *TPLOT
GOTO 8005
4010 OPEN (UNIT=8, NAME= 'DK:FE1.IO', TYPE= 'NEW', ERR=8000,
2ACCESS= 'SEQUENTIAL', FORM= 'FORMATTED')
TPLOT=10 *TPLOT
GOTO 8005
4020 OPEN (UNIT=8, NAME= 'DK:FE2.IO', TYPE= 'NEW', ERR=8000,
2ACCESS= 'SEQUENTIAL', FORM= 'FORMATTED')
TPLOT=500
GOTO 8005
4030 OPEN (UNIT=8, NAME= 'DK:FSH.IO', TYPE= 'NEW', ERR=8000,
2ACCESS= 'SEQUENTIAL', FORM= 'FORMATTED')
TPLOT=1000
GOTO 8005
4035 OPEN (UNIT=8, NAME= 'DK:FE3.IO', TYPE= 'NEW', ERR=8000,
2ACCESS= 'SEQUENTIAL', FORM= 'FORMATTED')
TPLOT=10 *TPLOT
GOTO 8005
4040 OPEN (UNIT=8, NAME= 'DK:FE4.IO', TYPE= 'NEW', ERR=8000,
2ACCESS= 'SEQUENTIAL', FORM= 'FORMATTED')
TPLOT=10 *TPLOT
GOTO 8005
4050 OPEN (UNIT=8, NAME= 'DK:FE5.IO', TYPE= 'NEW', ERR=8000,
2ACCESS= 'SEQUENTIAL', FORM= 'FORMATTED')
TPLOT=10 *TPLOT
GOTO 8005
4060 OPEN (UNIT=8, NAME= 'DK:FE6.IO', TYPE= 'NEW', ERR=8000,
2ACCESS= 'SEQUENTIAL', FORM= 'FORMATTED')
GOTO 8005
8005 WRITE (8,301) T, X0, V1
WRITE (8,301) C1, C3, C4
WRITE (8,301) G, X7, T1
WRITE (8,308) IR, K
CTOTAL=0.0
DO 3620 I = 2, K
WRITE (8, 306) C(I, I), I
3620 CTOTAL = CTOTAL + C(I, I)
CMean = CTOTAL / K
CLOSE (UNIT = 8, DISPOSE = 'SAVE', ERR = 8000)
3599 CONTINUE
3600 CONTINUE
.8000 WRITE (8, 501)
WRITE (8, 501)
.CLOSE (UNIT = 6, DISPOSE = 'SAVE', ERR = 8000)
GOTO 8009
C THIS IS THE PLO,T EXMPELE IN THE RT-11 BOOK
C ON PAGE 5-19
DELTAX = X0 / (IR - 2)
XMAX = 1.5 * X0
XMIN = X7 - .00003
YMIN = 0.0
MAXX = INT((XMAX - XMIN) / DELTAX)
MAXY = 72
YMAX = .01 * (INT(100 * X0 / K2) + 1)
WRITE (? , 205) XMIN, XMAX, YMAX, DELTAX
WRITE (? , 100) T, XOMIC, V1, C3PCT, C4PCT, CIPCT, VOLF, T1
DO 20 IX = 1, MAXX
IIX = IX
IXP1 = IX + 1
XP1 = SCAL (XMIN, XMAX, MAXX, IXP1)
X = SCAL (XMIN, XMAX, MAXX, IIX)
IXFLAG = 0
IF (XP1 .GE. X0 .AND. X .LE. X0) IXFLAG = 1
CALL REPEAT ('* ', STRING, MAXY)
IF (IIX .EQ. 1 .OR. IX .EQ. MAXX) GOTO 20
C(IR, I) = C3
REI = X * IR / X0
I = INT (REI)
IF (X .LE. X0) GOTO 5
REI = (X-X0) * (K-IR) / (G-X0) + IR
I = INT (REI)
C(IR, I) = C4
C(I, 1) = C(I, 1) + (REI-1) * (C(I+1, 1) - C(I, 1))
FUNX = C(I, 1)
DO 10 IY = 2, MAXY - 1
IIY = IY
IFUN = 1
INTF = FLOAT (MAXY) * (FUNX - YMIN) / (YMAX - YMIN)
IC3 = FLOAT (MAXY) * (C3 - YMIN) / (YMAX - YMIN)
IC4 = FLOAT (MAXY) * (C4 - YMIN) / (YMAX - YMIN)
IF (IIY .EQ. INTF) IFUN = 2
IF (IXFLAG .EQ. 1 .AND. IY .GE. IC4 AND. IY .LE. IC3) IFUN = 3
10 STRING (IY) = STAB (MINO (MAXF, MAX0(1, IFUN)))
20 CALL PUTSTR (7, STRING, ...)
CALL EXIT
WRITE(8, 501)
WRITE(7, 501)
END
APPENDIX V

CALCULATION OF THE TRANSFER OF CARBON BETWEEN PARTICLES

The correspondence between program variables and variables in the text is as follows:

<table>
<thead>
<tr>
<th>Program</th>
<th>Text</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>a</td>
</tr>
<tr>
<td>B</td>
<td>b</td>
</tr>
<tr>
<td>T7</td>
<td>time increment</td>
</tr>
<tr>
<td>A1</td>
<td>A₁</td>
</tr>
<tr>
<td>B1</td>
<td>B₁</td>
</tr>
<tr>
<td>L</td>
<td>X₂</td>
</tr>
<tr>
<td>L2</td>
<td>Y₂</td>
</tr>
<tr>
<td>C₁</td>
<td>Initially ( C_{1}^{SL} ) but becomes ( C_{1}^{L} )</td>
</tr>
<tr>
<td>C3</td>
<td>Initially ( T_{1}^{L} ) but becomes ( T_{1}^{L} )</td>
</tr>
<tr>
<td>Y1</td>
<td>( Y_{0} )</td>
</tr>
<tr>
<td>Y₀</td>
<td>( Y_{1} )</td>
</tr>
<tr>
<td>C2</td>
<td>Initially ( C_{1}^{SR} ) but becomes ( C_{1}^{R} )</td>
</tr>
<tr>
<td>C4</td>
<td>Initially ( T_{1}^{R} ) but becomes ( T_{1}^{R} )</td>
</tr>
<tr>
<td>J₁</td>
<td>( J_{1}^{α} )</td>
</tr>
<tr>
<td>T</td>
<td>Total time, ( t )</td>
</tr>
</tbody>
</table>

The integral in Eq. (2.46) is evaluated step-wise; thus the current value of \( T_{1}^{L} \) is derived from the old value of \( T_{1}^{L} \) by subtracting \( J₁ \times T₁ \). C7, C2, C3 and C4 are given by equations of the same form as Eqs. (2.43) to (2.46) but
involving current values of the variables involved (rather than initial values).

Eqs. (2.43b) and (2.46b) may be re-written using current values of $C_1^R$ and $T_R$ and substituting program variables:

$$C_2 = \frac{(A_1 + B_1 Y_1 - A)}{B}$$

$$C_{R1} = C_2(Y_1 - Y_0)$$

Eliminating $Y_1$ leads to a quadratic expression involving $C_2$ which is solved for each time increment.
46. \( a = 0.66814 \)
47. \( b = -1.44544 \)
48. \( c = -0.035 \)
49. \( d = 3.1 \)
50. \( e = 0.71 \)
51. \( f = -1.8 \)
52. \( g = 2.3 + 1 \)
53. \( h = 3.8 - 1 \)
54. \( i = 1.41 + 1 \)
55. \( j = 1.4 + 1 \)
56. \( k = 1.4 + 1 \)
57. \( l = 1.4 + 1 \)
58. \( m = 1.4 + 1 \)
59. \( n = 1.4 + 1 \)
60. \( o = 1.4 + 1 \)
61. \( p = 1.4 + 1 \)
62. \( q = 1.4 + 1 \)
63. \( r = 1.4 + 1 \)
64. \( s = 1.4 + 1 \)
65. \( t = 1.4 + 1 \)
66. \( u = 1.4 + 1 \)
67. \( v = 1.4 + 1 \)
68. \( w = 1.4 + 1 \)
69. \( x = 1.4 + 1 \)
70. \( y = 1.4 + 1 \)
71. \( z = 1.4 + 1 \)
APPENDIX VI

FINITE DIFFERENCE CALCULATION FOR THE GROWTH OF THREE AUSTENITE PARTICLES IN A LONG MANGANESE GRADIENT

Fig. 2.21 illustrates the initial conditions for calculating the manganese diffusion controlled growth of austenite particles in a long manganese gradient and defines a number of the variables. The material is divided into seven regions alternating ferrite and austenite. The variable names change systematically so that the detailed description of the calculation will be limited to the material between $X_o$ and $Y_o$. The point $X_I$ between $X_o$ and $Y_o$ is given by:

$$X_I = \frac{I - IX}{IY - IX} (Y_o - X_o) + X_o \quad (A6.1)$$

Differentiating with respect to time gives:

$$\frac{dX_I}{dt} = \frac{I-IX}{IY-IX} \frac{dY}{dt} + \frac{IY - I}{IY - IX} \frac{dX}{dt} \quad (A6.2)$$

$\frac{dC_I}{dt}$ is still given by Eqs. (A4.2) to (A4.4) using Eq. (A6.2) and with $F2$ given by:

$$F2 = F2XY = D^a_2 \left(\frac{IY - IX}{Y_o - X_o}\right)^2 \quad (A6.3)$$

The carbon concentration is assumed uniform within each austenite particle and interface concentrations have variable names of the type $C1U$, $C3U$, $C4U$ for $C_1$, $C_2^\gamma$ and $C_2^\gamma$, respectively. The last letter in the variable name is the letter associated with the left-most interface of the
particle, i.e., UW or Y.

The variable names in the program are related to variable in the text as for the program in Appendix IV with the following exceptions and additions.

<table>
<thead>
<tr>
<th>Program</th>
<th>Text</th>
</tr>
</thead>
<tbody>
<tr>
<td>C11(I)</td>
<td>$C^t_I$</td>
</tr>
<tr>
<td>C12(I)</td>
<td>$C^{t+1}_I$</td>
</tr>
<tr>
<td>CWX</td>
<td>$T_{WX}$</td>
</tr>
<tr>
<td>CYZ</td>
<td>$T_{YZ}$</td>
</tr>
<tr>
<td>FLUXXY</td>
<td>$J^{XY}_1$</td>
</tr>
<tr>
<td>SXY</td>
<td>$S^{-}_{XY}$</td>
</tr>
</tbody>
</table>

Other variable names are chosen systematically by varying the letter associated with each interface, e.g., $T_{UV}$ becomes $CUV$.

Boundary conditions from $X_o$ to $Y_o$ are set in the program just above statement 3300, i.e.:

\[
\begin{align*}
C11(IX) &= C4W \\
C11(IY) &= C4Y
\end{align*}
\]  

(A6.4a) \hspace{1cm} (A6.4b)

$VX$ and $VY$ are given by Fick's first law using a finite difference expression for $\frac{dC}{dx}$. Eq. (A4.2) is rearranged in program statement 3300 to derive $C12(I)$ from $C11(I)$.

The calculations for other regions of material, e.g., from $U_o$ to $V_o$, involve equations of the same form as (A6.1) to (A6.4).
Grid coarsening is undertaken to prevent instabilities in a similar manner to that described in Appendix IV (using subroutines with names like UV).
THIS FILE CALCULATES AUSTENITE GROWTH IN A MANGANESE
GRADIENT AND ALSO SETS UP OUTPUT FOR THE CGRAPH.FOR
PROGRAM.

EDIT DIMENSION LINE TO BE CONSISTENT WITH K!

REAL X0, X1, X2, MO, L
COMMON/BLOCK1/C11(1005)/BLOCK2/IU, IV, IW, IX, IY, IZ, K, U0, V0, W0
 2, X0, Y0, Z0/BLOCK3/C12(1005)/BLOCK4/DELUV, WAVE, C3U, C4U, C3W, C4W,
 3C3Y, C4Y
C2D(X) = .0101 - 0.0035*COS(314.16*X)
C CONSTANT INSIDE COS IS PI/WAVE
OPEN (UNIT=6, NAME='DK:GRAD2.OUT', ERR=8000)
100 FORMAT(3E11.4, 3F10.5)
101 FORMAT('T1 REDUCED ')  
121 FORMAT(' MEAN CONC = ', F9.3)
205 FORMAT('0 XMIN= ',E9.2,' XMAX= ',E9.2,' MAX CONC= ',F8.5,' DEL  
 2 X= ',E9.2)
300 FORMAT(6F11.4)
301 FORMAT(6E12.4)
302 FORMAT(6F11.4)
303 FORMAT(' FLUXVW= ',E11.2,' FLUXXY= ',E11.2)
304 FORMAT(' OK ')  
305 FORMAT(' KS ARE ',3F9.4)
306 FORMAT(F9.6,19)
307 FORMAT(' TIME THEN TI ARE: ',2F15.2)
308 FORMAT(7I8)
309 FORMAT('0 OUTPUT OK AVERAGE CONC = ',F8.5)
310 FORMAT(F12.2,F9.6)
311 FORMAT(' INPUT/OUTPUT ERROR ENCOUNTERED ')  
333 FORMAT('0 PROGRAM PROPERLY TERMINATED ')  
340 FORMAT(' PARTICLE UV REMOVED, IZAP SET TO 1 ')  
1000 K=1000
101 IUFG=0
102 IUVFG=0
103 IVWFG=0
104 IWXFG=0
105 IYXFG=0
106 IZKFG=0
107 FG=0
108 IZAP=0
109 KFLAG=1
110 T=0
112 T10=.1
2000 P=K+1
201 FGRID=.75
202 D1=1.6E-6
203 TPC=0.1
TP=0.0
TPLOT=1.0
ICMIN=30
3000 DJ=1.0E-14
3010 D2=1.8E-12
3020 T1=1
TCE=.005
3030 K0=1.0297
3040 K1=0.027
3050 K2=0.336
3060 C0=0.0325 BULK CARBON AT%
3070 CB=0.00387 EUTECTOID CARBON AT%
3080, H0=0.0101 BULK MANGANESE
3090, UL=0.0001 AUSTENITE HALF WIDTH
WL=1.12*UL
YL=1.24*UL
WAVE=.01
SVW=.25*(WAVE-UL-WL-YL)
SXY=SVW
U0=SVW
V0=V0+UL
W0=W0+SVW
X0=X0+WL
YO=Y0+SXY
Z0=Y0+YL
3110 A=(K0-1.0)/(K0-K2)
3120 B=(K1-K0)/(K0-K2)
C1X=(C2D(Z0)-A)/B
C1W=C1X
C1U=C1Y
IU=INT(K*U0/WAVE)
IV=INT(K*V0/WAVE)
IW=INT(K*W0/WAVE)
IX=INT(K*X0/WAVE)
IY=INT(K*Y0/WAVE)
IZ=INT(K*Z0/WAVE)
CUV=C1U*(V0-U0)
CYZ=C1Y*(Z0-Y0)
CWX=C1W*(X0-W0)
DELX0=WAVE/K
DELUV=.2*DELX0
C3U=A+B*C1U
C3W=A+B*C1W
C3Y=A+B*C1Y
C4U=K2*C3U
C4W=K2*C4W
WRITE(6,305)K0,K1,K2
WRITE(7,305)K0,K1,K2
C4Y=K2*C3Y
U0MIC=10000.*U0
VOMIC=10000.*V0
VOMIC=10000.*W0
YOMIC=10000.*X0
ZOMIC=10000.*Z0
C3UPCT=100.*C3U
C3WPCT=100.*C3W
C3YPCCT=100.*C3Y
C1UPCT=100.*C1U
C1WPCT=100.*C1W
C1YPCCT=100.*C1Y
WRITE(6,300)VOMIC,VOMIC,VOMIC,XOMIC,YOMIC,ZOMIC
WRITE(7,300)UOMIC,VOMIC,VOMIC,XOMIC,YOMIC,ZOMIC
WRITE(7,301)UU,VV,VW,VX,VY,VZ
WRITE(6,302)C3UPCT,C1UPCT,C3WPCT,C1WPCT,C3YPCT,C1YPCT
WRITE(7,302)C3UPCT,C1UPCT,C3WPCT,C1WPCT,C3YPCT,C1YPCT
WRITE(6,303)FLUXVW,FLUXXY
WRITE(7,303)FLUXVW,FLUXXY
WRITE(6,308)IU,IV,IW,IY,IZ,K
WRITE(7,308)IU,IV,IW,IY,IZ,K
3170 DO 3200 I=1,K
3200 CI1(I)=C2D(I*WAVE/K)
DO 3201 I=IU,IV
3201 WRITE(7,306)CI1(I),I
DO 13601 IBB=1,3
3235 DO 13599 IB=1,10000
1 IF (IZAP.EQ.1) GOTO 3236
VW=(D2*(IW-IU)*(4*CI1(IW+1)-3.*C4W-CI1(IW+2)))/(2.*U0-V0)-E
2*(IV-IU)*(3.*C4U-4*CI1(IV-1)+CI1(IV-2))/(2.*(V0-U0)))/(C3U-C4U)
VV=(-D2*(IU-2)*(4*CI1(IU-1)-3.*C4U-CI1(IU-2)))/(2.*(U0-D4*)
2*(IV-IU))/(3.*C4U-4*CI1(IU+1)+CI1(IU+2))/(2.*(U0-D4*)
(VU=-(D2*(IW-IU)*(4*CI1(IW-1)-3.*C4W-CI1(IW-2)))/(2.*(W0-V0))
2*(IX-IW)*(3.*C3W-4*CI1(IX+1)+CI1(IX+2))/(2.*(X0-W0)))/(C3W-C4W)
VX=(D2*(IX-IX)*(4*CI1(IX+1)-3.*C4W-CI1(IX+2)))/(2.*(X0-D4*)
2*(IX-IW)*(3.*C3W-4*CI1(IX-1)+CI1(IX-2))/(2.*(X0-W0)))/(C3W-C4W)
VY=(D2*(IX-IX)*(4*CI1(IX-1)-3.*C4Y-CI1(IX-2)))/(2.*(Y0-X0))
2*(IZ-IY)*(3.*C3Y-4*CI1(IY+1)+CI1(IY+2))/(2.*(Z0-Y0)))/(C3Y-C4Y)
VZ=(D2*(IX-IX)*(4*CI1(IY-1)-3.*C4Y-CI1(IY-2)))/(2.*(WAVE-Z0))-
2*(IZ-IY)*(3.*C3Y-4*CI1(IY-1)+CI1(IY-2))/(2.*(Z0-Y0)))/(C3Y-C4Y)
CI1(I)=CI1(2)
IF (IZAP.EQ.1) GOTO 3285
C11(IU)=C4U
FU=D2*(IU-2)*(IU-2)/(U0-U0)
DO 3260 I=2,IU-1
3260 CI2(I)=(C11(I)-C11(I-1))/2.*FU
2*(C11(I-1)-2.*CI1(I)+CI1(I+1))*T1+CI1(I)
C11(IU)=C3U
C11(IV)=C3U
FU=FU-D4*(IV-IU)*(IV-IU)/(V0-U0)*(V0-U0)
DO 3270 I=IU+1,IV-1
3270  C12(I) = (((I-U) * VV/(V0-U0) + (IV-I) * VU/(V0-U0)) * (C11(I+1)
2-C11(I-1))/2 + F2UV*(C11(I-1) - 2 * C11(I) + C11(I+1)))*T1+C11(I)
C11(I) = C4U
C11(IW) = C4W
F2UV = D2 * (IV-IW) * (IW-IV)/(V0-V0) * (W0-V0)
DO 3280 I = IV-1, IV
3280  C12(I) = (((I-IV) * VW/(W0-V0) + (IW-I) * VV/(W0-V0)) * (C11(I+1)
2-C11(I-1))/2 + F2VV*(C11(I-1) - 2 * C11(I) + C11(I+1)))*T1+C11(I)
GOTO 3289
3285  C11(IW) = C4W
F20W = D2 * (IW-2) * (IW-2) / (W0*W0)
DO 3286 I = 2, IW-1
3286  C12(I) = (((I-2) * VW/(W0)) * (C11(I+1) - C11(I-1))/2 + F20W
2 * (C11(I-1) - 2 * C11(I) + C11(I+1)))*T1+C11(I)
3289  C11(IW) = C3W
C11(I) = C3W
F2WX = D4 * (IX-IW) * (IX-IW)/(X0-W0) * (X0-W0)
DO 3290 I = IW+1, IX
3290  C12(I) = (((IX-IW) * VX/(X0-W0) + (IX-I) * VW/(X0-W0)) * (C11(I+1)
2-C11(I-1))/2 + F2WX*(C11(I-1) - 2 * C11(I) + C11(I+1)))*T1+C11(I)
G11(IX) = C4W
C11(IY) = C4Y
F2XY = D2 * (IY-IX) * (IY-IX)/(Y0-X0) * (Y0-X0)
DO 3300 I = IX+1, IY-1
3300  C12(I) = (((IX-I) * VX/(Y0-X0) + (Y0-IY) * VX/(Y0-X0)) * (C11(I+1)
2-C11(I-1))/2 + F2XY*(C11(I-1) - 2 * C11(I) + C11(I+1)))*T1+C11(I)
C11(IY) = C3Y
C11(IZ) = G3Y
F2YZ = D4 * (IZ-IY) * (IZ-IY)/(Z0-Y0) * (Z0-Y0)
DO 3310 I = IY+1, IZ-1
3310  C12(I) = (((IZ-IY) * VZ/(Z0-Y0) + (IZ-I) * VY/(Z0-Y0)) * (C11(I+1)
2-C11(I-1))/2 + F2YZ*(C11(I-1) - 2 * C11(I) + C11(I+1)))*T1+C11(I)
C11(IZ) = C4Y
C11(I) = C11(K)
F22Z = D2 * (K-I) * (K-I)/(WAVE-Z0) * (WAVE-Z0)
DO 3320 I = IZ+1, K
3320  C12(I) = (((K-I) * VZ/(WAVE-Z0)) * (C11(I+1)
2-C11(I-1))/2 + F22Z*(C11(I-1) - 2 * C11(I) + C11(I+1)))*T1+C11(I)
3450  DO 3460 I = 2, K
3460  C11(I) = C12(I)
3470  T = T+1
3475  X0 = X0 + T1 * VX
U0 = U0 + T1 * VU
V0 = V0 + T1 * VW
W0 = W0 + T1 * VW
X0 = X0 + T1 * VX
Y0 = Y0 + T1 * VY
Z0 = Z0 + T1 * VZ
IF (TCF.LE.001*T1) TCF = 001*T1
KCF = INT(T1/TCF)
DO 3484 KC=1,KCF
FLUX(V)=D1*K1*(C1U-C1W)/SVV
FLUXXY=D1*K1*(C1W-C1Y)/SXY
IF (IZAP.EQ.1) FLUX(V)=0
CWX=CWX+FUX(V)-FLUXXY*TI/KCF
CYZ=CYZ+FLUXXY*TI/KCF
C1W=CWX/(X0-V0)
CUV=CUV-FLUXV*TI/KCF
C1U=CUV/(V0-U0)
C1Y=CYZ/(Z0-Y0)
SVV=W0-V0
SXY=Y0-X0
C3W=A+B*C1W
C3Y=A+B*C1Y
C4W=K2*C3W
C4Y=K2*C3Y.
IF (IZAP.EQ.1) GOTO 3486
C3U=A+B*C1U
C4U=K2*C3U
C
C
3486 IF (T .GT. 200000.) GOTO 8002
IF ((V0-U0) LT (3.*DELX0)) AND (IZAP.EQ.0) GOTO 3480
IF (T .GT. TP) GOTO 3480
GOTO 3493
3480 C3UPCT=100.*C3U
C3WPCT=100.*C3W
C3YPCT=100.*C3Y
C1UPCT=100.*C1U
C1WPCT=100.*C1W
C1YPCT=100.*C1Y
U0MIC=10000.*U0
V0MIC=10000.*V0
W0MIC=10000.*V0
X0MIC=10000.*X0
Y0MIC=10000.*Y0
Z0MIC=10000.*Z0
WRITE(7,307) T, TI
WRITE(6,307) T, TI
WRITE(7,300) U0MIC, V0MIC, W0MIC, X0MIC, Y0MIC, Z0MIC
WRITE(6,300) U0MIC, V0MIC, W0MIC, X0MIC, Y0MIC, Z0MIC
WRITE(7,301) VU, VV, VX, VY, VZ
WRITE(6,301) VU, VV, VX, VY, VZ
WRITE(7,302) C3UPCT, C1UPCT, C3WPCT, C1WPCT, C3YPCT, C1YPCT
WRITE(6,302) C3UPCT, C1UPCT, C3WPCT, C1WPCT, C3YPCT, C1YPCT
WRITE(7,303) FLUX(V), FLUXXY
WRITE(6,303) FLUX(V), FLUXXY
WRITE(7,308) IU, IV, IW, IX, IV, IZ, K
WRITE(6,308) IU, IV, IW, IX, IV, IZ, K
IF ((V0-U0) LT (3.*DELX0)) AND (IZAP.EQ.0) GOTO 5011
IF(X0 .LE. 0.0) GOTO 8002
TP=TP+TPC
IF(T .GE. TPL0T) GOTO 13600
IF(T .GE. (10*TPC)) GOTO 3492
GOTO 3493
3492
IF(TPC .GE. 10000.) GOTO 3493
TPC=10.0*TPC
3493
T10=T1
FT= .01
IF(KFLAG EQ 0) GOTO 13599
IF(T1 .GE. (0.15/F2U)) AND. IUVF. EQ. 1) GOTO 13599
IF(T1 .GE. (0.15/F2UV)) AND. IUVF. EQ. 1) GOTO 13599
IF(T1 .GE. (0.15/F2VW)) AND. IYWFG. EQ. 1) GOTO 13599
IF(T1 .GE. (0.15/F2WX)) AND. IWXFG. EQ. 1) GOTO 13599
IF(T1 .GE. (0.15/F2XY)) AND. IXYFG. EQ. 1) GOTO 13599
IF(T1 .GE. (0.15/F2ZK)) AND. IZKFG. EQ. 1) GOTO 13599
IF(T1 .LE. (FT*T)) T1=FT*T
IF(T1 .GE. 15.) T1=15.
IF(T1 .GT. (.2/F2UV) AND. IZAP. EQ. 0) CALL GRIDUV
IF(T1 .GT. (.2/F2WX) CALL GRIDWX
IF(T1 .GT. (.2/F2ZK) CALL GRIDZK
IF(T1 .GT. (.2/F2XY) CALL GRIDXY
IF(T1 .GT. (.2/F2U) AND. IZAP. EQ. 0) CALL GRIDU
GOTO 13599
C
C
13600
IF(T GT 10000.) GOTO 4060
IF(T GT 10000.) GOTO 4050
IF(T GT 10000.) GOTO 4040
IF(T GT 10000.) GOTO 4035
IF(T GT 500.) GOTO 4030
IF(T GT 100.) GOTO 4020
IF(T GT 10.) GOTO 4010
IF((V0-60.)LT.(3.*DELX0)) AND. IZAP. EQ. 0) GOTO 4080
OPEN(UNIT=8, NAME='DK:TE1.IO', TYPE='NEW', ERR=8000, 2ACCESS='SEQUENTIAL',FORM='FORMATTED')
TPL0T=10 *TPL0T
GOTO 8003
4010 OPEN(UNIT=8, NAME='DK:TE2.IO', TYPE='NEW', ERR=8000, 2ACCESS='SEQUENTIAL',FORM='FORMATTED')
TPL0T=10 *TPL0T
GOTO 8005
4020 OPEN(UNIT=8, NAME='DK:TE3.IO', TYPE='NEW', ERR=8000, 2ACCESS='SEQUENTIAL',FORM='FORMATTED')
TPL0T=500
GOTO 8005
4030 OPEN(UNIT=8, NAME='DK:TSH.IO', TYPE='NEW', ERR=8000, 2ACCESS='SEQUENTIAL',FORM='FORMATTED')
TPL0T=1000
GOTO 8005
OPEN (UNIT=8, NAME='DK:TE3.IO', TYPE='NEW', ERR=8000, ACCESS='SEQUENTIAL', FORM='FORMATTED')
TPlot=10 * TPlot
GOTO 8005

OPEN (UNIT=8, NAME='DK:TE4.IO', TYPE='NEW', ERR=8000, ACCESS='SEQUENTIAL', FORM='FORMATTED')
TPlot=10 * TPlot
GOTO 8005

OPEN (UNIT=8, NAME='DK:TE5.IO', TYPE='NEW', ERR=8000, ACCESS='SEQUENTIAL', FORM='FORMATTED')
TPlot=10 * TPlot
GOTO 8005

OPEN (UNIT=8, NAME='DK:TE6.IO', TYPE='NEW', ERR=8000, ACCESS='SEQUENTIAL', FORM='FORMATTED')
TPlot=10 * TPlot
GOTO 8005

IZAP=2
GOTO 8005

OPEN (UNIT=8, NAME='DK:AZ.IO', TYPE='NEW', ERR=8000, ACCESS='SEQUENTIAL', FORM='FORMATTED')
WRITE(8,310)T,WAVE
WRITE(8,301)U0,V0,W0,X0,Y0,Z0
WRITE(8,301)VU,VV,VW,VX,VY,VZ
WRITE(8,301)C3U,C1U,C3W,C1W,C3Y,C1Y
WRITE(8,306)U1,IV,1W,IX,1Y,IZ,K
C TOTAL=0,0
DO 3620 I=2,K
WRITE(8,306)C11(I),I
C TOTAL=C TOTAL+C12(I)
C MEAN=C TOTAL/K
CLOSE(UNIT=8,DISPOSE='SAVE',ERR=8000)
IF(I ZAP .EQ. 2)GOTO 5011
GOTO 13599

C
C SECTION FOR DESTROYING PARTICLE UV
C

IF(I ZAP .EQ. 0)GOTO 4080
WRITE(6,340)
34501 DO 34601 I=2,K
34601 C12(I)=C11(I)
WRITE(7,340)
C12(1U)=.5*(C3U+C4U)
C12(1W)=C4W
C12(1V)=C12(1U)
IZAP=1
C12(1)=C12(2)
DO 5111 I=2,1W-1
X1=FLOAT(I-2)*W0/FLOAT(1W-2)
IF(X1 LT.U0) RE1=X1*(1U-2)/U0+2.
IF(XI GT U0 AND XI LT V0) REI=(XI-U0)*(IV-IU)/(V0-U0)+IU
IF(XI.GT V0) REI=(XI-V0)*(IW-IV)/(W0-V0)+IV
IF(XI.EQ V0) REI=FLOAT(IU)
IF(XI.EQ U0) REI=FLOAT(IU)
IO=INT(REI)
C11(I)=C12(IO)+(REI-IO)*(C12(IO+1)-C12(IO))
5111 WRITE(7,345)I,IO,C11(I),C12(IO),REI
DO 5112 I=IW+1,K
5112 C11(I)=C12(I)
345 FORMAT(2I8,3E12.5)
GOTO 4098
13599 CONTINUE
13601 CONTINUE
GOTO 8001
8000 WRITE(7,311)
WRITE(6,311)
GOTO 8002
8001 WRITE(7,309)CMEAN
WRITE(6,309)CMEAN
8002 WRITE(6,333)
WRITE(7,333)
CLOSE(UNIT=6,DISPOSE='SAVE',ERR=8000)
END
SUBROUTINE GRIDU
COMMON/BLOCK1/C11(1005)/BLOCK2/ IU, IV, IW, IX, IY, IZ, K, U0, V0, W0
2, X0, Y0, Z0/BLOCK3/C12(1005)/BLOCK4/DELV, WAVE, C3U, C4U, C3W, C4W,
3C0Y, C4Y
WRITE(7,401)
401 FORMAT('GRID 0 TO U0 COARSEND')
3450 DO 3460 I=2,K
3460 C12(I)=C11(I)
FGRID= 0.8
IUN=INT(FGRID*(IU-2))+2
DELX0=10*DELV
IF((IU/(IU-2)) .GT. DELX0) GOTO 3580
GOTO 3560
3580 IUN=INT(U0/DELX0)+2
IUFG=1
3560 TGRID=FLOAT(IUN-2)/FLOAT(IU-2)
C12(IU)=C4U
DO 3570 I=2,IUN
REI=(I-2)/TGRID+2.
IO=INT(REI)
3570 C11(IO)=C12(IO)+(REI-IO)*(C12(IO+1)-C12(IO))
IRED=IU-IUN
K=K-IRED
DO 3575 I=IUN+1,K
IO=I+IRED
3575 C11(I)=C12(IO)

POOR COPY
IU=IUN
IX=IX-IRED
IY=IY-IRED
IZ=IZ-IRED
IV=IV-IRED
IW=IW-IRED

310 FORMAT(F8.4)
308 FORMAT(7I8)
WRITE(7,308)IU,IY,IX,IY,IZ,K
RETURN
END

SUBROUTINE GRIDUV
COMMON/BLOCK1/C11(1005)/BLOCK2/IU,IY,IX,IZ,K,U0,V0,W0
2,X0,Y0,Z0/BLOCK3/C12(1005)/BLOCK4/DELUV,WAVE,C3U,C4U,C3W,C4W,
3C3Y,C4Y
402 FORMAT("
GRID U0 TO V0 COARSENGED"
)
444 FORMAT("
MAXIMUM GRID SPACING OF UV GRID ENCOUNTERED"
)
3450 DO 3460 I=2,K
3460 C12(I)=C11(I)
WRITE(7,402)
FGRID=.8
IVN=INT(FGRID*(IV-IU))+IU
IF((V0-U0)/((IVN-IU)) .GT. DELUV) GOTO 3580
GOTO 3585
3580 IF((INT((V0-U0)/DELUV)+IU) .GT. IVN) GOTO 3585
IVN=INT((V0-U0)/DELUV)+IU
WRITE(7,444)
IUVFG=1
3585 FGRID=FLOAT(IVN-IU)/FLOAT(IV-IU)
C12(IU)=C3U
C12(IY)=C3U
DO 3586 I=IU,IVN
REI=(I-IU)/FGRID+IU
IO=INT(REI)
3586 C11(I)=C12(IO)+(REI-IO)*(C12(IO+1)-C12(IO))
IRED=IV-IVN
K=K-IRED
DO 3587 I=IVN+1,K
IO=I+IRED
3587 C11(I)=C12(IO)
IW=IW-IRED
IV=IVN
IX=IX-IRED
IY=IY-IRED
IZ=IZ-IRED
310 FORMAT(F8.4)
308 FORMAT(7I8)
WRITE(7,308)IU,IY,IX,IZ,K
RETURN
END
SUBROUTINE GRIDWX
COMM/ BLOCK1/C11(1005)/ BLOCK2/ IU, IV, IW, IX, IY, IZ, K, U0, V0, W0
2, X0, Y0, Z0/ BLOCK3/C12(1005)/ BLOCK4/ DELUV, WAVE, C3U, C4U, C3W, C4W,
3C3Y, C4Y
WRITE(7,403)
 FORMAT( ', ,GRID FROM W0 TO X0 COARSENEO ', )
403 DO 3460 I = 2, K
3460 CI2(I) = CI1(I)
 FGRID = 8
 IXN = INT(FGRID*( IX-IW )+ IW
 IF((X0-W0)/(IXN-IW)) .GT. DELUV GOTO 3580
 GOTO 3585
3580 IF((INT((X0-W0)/DELUV)+IW) .GT. IXN) GOTO 3585
 IXN = INT((X0-W0)/DELUV)+IW
 IWFG = 1
3585 FGRID = FLOAT(IXN-IW)/FLOAT(IX-IW)
 CI2(IW) = C3W
 CI2(I) = C3W
 DO 3586 I = IW, IXN
3586 REI = (I-IW)/FGRID+IW
 IO = INT(REI)
3586 CI1(I) = CI2(IO)+(REI-IO)*(CI2(IO+1)-CI2(IO))
 IRED = IX-IWN
 K = K-IRED
 DO 3587 I = IXN+1, K
3587 IO = I+IRED
3587 CI1(I) = CI2(IO)
 IX = IXN
 IY = IY-IRED
 IZ = IZ-IRED
310 FORMAT(F8.4)
308 FORMAT(718)
 WRITE(7,308) IU, IV, IW, IX, IY, IZ, K
 RETURN
END
SUBROUTINE GRIDVW
COMM/ BLOCK1/C11(1005)/ BLOCK2/ IU, IV, IW, IX, IY, IZ, K, U0, V0, W0
2, X0, Y0, Z0/ BLOCK3/C12(1005)/ BLOCK4/ DELUV, WAVE, C3U, C4U, C3W, C4W,
3C3Y, C4Y
 WRITE(7,404)
404 FORMAT( ', ,GRID FROM V0 TO W0 COARSENEO ', )
3450 DO 3460 I = 2, K
3460 CI2(I) = CI1(I)
 FGRID = 8
 IWN = INT(FGRID*( IW-IV))+ IV
 DELX0 = 10.*(DELUV
 IF((W0-V0)/(IWN-IV)) .GT. DELX0 GOTO 3580
 GOTO 4003
3580 IWN = INT((W0-V0)/DELX0)+ IV
 IVWFG = 1
FGRID=FLOAT(IWN-IV)/FLOAT(IW-IV)
C12(IV)=C4V
C12(IW)=C4W
DO 4006 I=IV,IWN
REI=(I-IV)/FGRID+IV
IO=INT(REI)
4006 C11(I)=C12(IO)+(REI-IO)*(C12(IO+1)-C12(IO))
IRED=IV-IVN
K=K-IRED
DO 4007 I=IVN+1,K
IO=I+IRED
4007 C11(I)=C12(IO)
IW=IVN
IX=IX-IRED
IY=IY-IRED
IZ=IZ-IRED
310 FORMAT(F8.4)
308 FORMAT(7I8)
WRITE(7,308)IU,IV,IW,IX,IY,IZ,K
RETURN
END
SUBROUTINE GRIDXY
COMMON/BLOCK1/C11(1005)/BLOCK2/IU,IV,IW,IX,IY,IZ,K,U0,V0,W0
2,X0,Y0,Z0/BLOCK3/C12(1005)/BLOCK4/DELUV,WAVE,C3U,C4U,C3W,C4W,
3C3Y,C4Y
WRITE(7,405)
FORMAT(", GRID FROM X0 TO Y0 COARSENERED")
3450 DO 3460 I=2,K
3460 C12(I)=C11(I)
310 FORMAT(F8.4)
308 FORMAT(7I8)
FGRID=IYN
IYN=INT(FGRID*(IY-IX))+IX
DELX0=10.*DELUV
IF((Y0-X0)/(IYN-IX)) .GT. DELX0) GOTO 3580
GOTO 4012
3580 IYN=INT((Y0-X0)/DELX0)+IX
IYFG=1
4012 FGRID=FLOAT(IYN-IX)/FLOAT(IY-IX)
C12(IX)=C4W
C12(IY)=C4Y
DO 4016 I=IX,IYN
REI=(I-IX)/FGRID+IX
IO=INT(REI)
4016 C11(I)=C12(IO)+(REI-IO)*(C12(IO+1)-C12(IO))
IRED=IY-IYN
K=K-IRED
DO 4007 I=IYN+1,K
IO=I+IRED
4007 C11(I)=C12(IO)
IY = IYN
IZ = IZ - IRED
WRITE (7, 306) IU, IY, IW, IX, IY, IZ, K
RETURN

2ND
SUBROUTINE GRIDZK
COMMON/ BLOCK1/C11(1005)/ BLOCK2/IU, IY, IW, IX, IY, IZ, K, U0, V0, W0, X0, Y0, Z0 / BLOCK3/C12(1005)/ BLOCK4/ DELUV, WAVE, C3U, C4U, C3W, C4W, 3C3Y, C4Y
WRITE (7, 406)
FORMAT(' GRID FROM Z0 TO END COARSENED')
DO 3460 I = 2, K
3450 C12(I) = CI1(I)
3460 FGRID = 8
KN = INT(FGRID * (K - IZ)) + IZ
DELSO = 10. * DELUV
IF ((WAVE - Z0) / (KN - IZ)) < GT. DELX0) GOTO 3580
GOTO 4012
3580 KN = INT((WAVE - Z0) / DELX0 + IZ)
IZKFG = 1
4012 FGRID = FLOAT(KN - IZ) / FLOAT(K - IZ)
C12(IZ) = C4Y
C12(K + 1) = C12(K)
IRED = K - KN
K = K - IRED
DO 4016 IO = IZ, KN
RE1 = (I - IZ) / FGRID + IZ
IO = INT(RE1)
4016 CI1(IO) = C12(IO) + (RE1 - IO) * (C12(IO + 1) - C12(IO))
310 FORMAT (F8.4)
308 FORMAT (718)
WRITE (7, 308) IU, IY, IW, IX, IY, IZ, K
RETURN
END
APPENDIX VII

CALCULATION OF ALLOYING ELEMENT DIFFUSION
CONTROLLED GROWTH FOR QUATERNARY Fe-C-Mn-Si

The manganese and silicon mass balances are solved using concentration profiles similar to the one shown schematically in Fig. A7. The variables X7, X2, MI, M2 and M4 are defined in Fig. A1. There is the following correspondence between program variables and variables in the text.

<table>
<thead>
<tr>
<th>Program</th>
<th>Text</th>
</tr>
</thead>
<tbody>
<tr>
<td>X7</td>
<td>X_S</td>
</tr>
<tr>
<td>C7</td>
<td>C_1</td>
</tr>
<tr>
<td>A</td>
<td>a</td>
</tr>
<tr>
<td>B</td>
<td>b</td>
</tr>
<tr>
<td>S1</td>
<td>C_3^γ (cf. M1 in Fig. A7)</td>
</tr>
<tr>
<td>S2</td>
<td>C_3^α (cf. M2 in Fig. A7)</td>
</tr>
<tr>
<td>S4</td>
<td>∫_X_S X_0 C_3^γ - C_3^α dX (cf. M4 in Fig. A7)</td>
</tr>
<tr>
<td>X</td>
<td>X_0</td>
</tr>
<tr>
<td>S7</td>
<td>C_3^αI</td>
</tr>
<tr>
<td>M7</td>
<td>C_2^αI</td>
</tr>
</tbody>
</table>

The program proceeds by decreasing the carbon concentration (line 420) thus determining a new interface position (line 430). Lines 460 to 1020 then iterate to find a new interface silicon concentration Si such that interface velocities based on manganese flux and silicon flux, are equal.
10 REM 11:13:15:17
20 FORMAT (F8.5, 5E10.3)
30 M1=1E-10
40 DATA 0.027, 1.0, 0.336, 1.02, 7
50 DATA 0.0325, 0.01, 9.0, 1.0102
60 N4=M4=T=0
70 READ D3, D2, L1
100 DATA 3.4E-11, 2.2E-13, 0.006
110 M3=M0
120 M1=M0
130 F3=F3=0
140 T=10, 12
150 T6=T7=0, 01
160 D4=1E-14
170 D6=1E-14
180 S5=S0
190 A=K0-1, 2
200 B0=K1+0, 1
210 C0=K3+0, 2
220 C7=(M0-A-L+0, 10, 2, 0)
230 PRINT "QUARTERHAYY CALCULATION"
240 D=L-400, 89
250 PRINT
260 PRINT "SO"="50", M0="M0", D5="D5", Dm="Dm"
270 PRINT "A="="B", E="C", C="L"
280 PRINT "F1="="T", F2="F2", F3="F3", F4="F4"
290 PRINT "BULI CAPB="="B9", D5 IM, GAMMA="="D5", MN, GAMMA="="D5"
300 PRINT
310 C1=C7
320 C0=CO-L-C1
330 D9=0.000005
340 D8=N7
350 S1=S0
360 S=-1E-06
370 PRINT "CALCULATION DELTA C1="="D9", D="D"
380 PRINT
390 PRINT "CAPB SI MN TIME VOL FPAC F2"
400 PRINT
410 FOR J=1 TO 18WU
420 M8=M9
430 M9=M1
440 N8=N1
450 C1=C1-D9
460 N8=C0-L-C1
470 T1=X+X
480 S5=S1
490 FOR I=1 TO 15
500 S1=S+S3
510 GOTO 520
520 S3=1E-05

1969 IF R3 LE 30 THEN 10 M
1970 NEXT T
1971 IF R3 LE 30 THEN 1300
1972 IF N2 MA THEN 1100
1973 N S1 S2 S3
1974 IF S1+S2 S0=S THEN 1070
1975 GOTO 1060
1976 S3=S2
1977 S1=S0-K4
1978 PRINT "S1=" S1
1979 GOTO 450
1980 IF M3=M0 THEN 180
1981 V2=X
1982 S4=S4+51-80+41
1983 M4=M4-(M1-00+X)
1984 GOTO 690
1985 V3=Y8+V2+2+43
1986 T1=X-Y8-V3
1987 W5=W1
1988 P1=-P1-V3+1-50
1989 P2=2-V6+M1-M0
1990 V1=M4-M1-M6+118+111-11.8
1991 IF V1=V3 THEN 1350
1992 I=I+1
1993 GOTO 420
1994 D9=0.5+09
1995 IF T TO THEN 1210
1996 GOTO 1310
1997 IF F=1 THEN 1,54
1998 IF F=1 THEN 4,576
1999 WRITE 1550 "THE MAJOR PROBLEM IS..."
2000 GOTO 1280
2001 WRITE 1320 "LIKE 20+L1+81-M1."
2002 GOTO 1380
2003 WRITE 1300 "LIKE 15, 20, 1, 31-M1, T5-T7."
2004 T6=T5+7
2005 T8=10+T7
2006 IF T8 TO THEN 1300
2007 GOTO 1310
2008 T7=T8
2009 NEXT T
2010 PRINT "ITERATION: PROBLEM MAGNITUDE"
APPENDIX VIII
CONVOLUTION CALCULATION FOR THE ELECTRON MICROPROBE

For the specimen annealed 50 h at 750°C, the concentration profile associated with the end of growth was expected (cf. Fig. 2.6c). For the convolution calculation, the slight gradient in the ferrite was neglected. The convolution integral may be written:

\[
F(T) = \int_{-\infty}^{\infty} G(x-T) \ C(X) \, dt
\]

(A8.1)

The "base level" of manganese \( C_4 = C_2^{\gamma} \) may be separated to give:

\[
F(T) = \int_{-\infty}^{\infty} G(x-T) \ C_4 \, dt \int_{-\infty}^{\infty} G(x-T) (C(X) - C_4) \, dt
\]

(A8.2)

\( C(X) \), as may be seen in Fig. 2.6c, is symmetrical about \( x=0 \). Variables \( x_{s} \) and \( x_{p} \) are changed to \( A \) and \( B \). The first integral on the right-hand side of (A8.2) simply returns \( C_4 \) while the second integral may be separated into three definite integrals since it is zero everywhere except for the region from \(-B\) to \( B \). Thus:

\[
F(T) = C_4 + \int_{-B}^{A} (C_2^{\gamma}(X) - C_4) \ G(x-t) \, dt
\]

\[
+ \int_{-A}^{A} (C_2 - C_4) \ G(x-t) \, dt
\]

\[
+ \int_{A}^{B} (C_2^{\gamma}(X) - C_4) \ G(x-t) \, dt
\]

= \( C_4 + I_1 + I_2 + I_3 \)

The following section of computer program evaluates \( I_1, I_2 \) and \( I_3 \) numerically. Remark statements in lines 1380
to 1470 explains the details of the calculation for evaluating \( I_1 \) while \( I_2 \) and \( I_3 \) proceed in a similar manner.
650 PRINT
660 T=0.00000000
670 PRINT "F: T="; "I1","I2","I3"
680 PRINT
690 REM SET INITIAL VALUES FOR INTEGRATION TO GET I1
700 t1=0
710 I1=0
720 "="-A.
730 T1=0
740 J1=-1+PI+(1-T); D/2.4
750 IF J1<-1-14 THEN 830
760 S1=(C2-C4)+EXP(J1)*(2+D)
770 REM TRAPEZOIDAL RULE OF INTEGRATION, EVALUATE
780 REM-- THE INCREMENT OF I1, T1 IS THE PREVIOUS VALUE.
790 REM-- OF THE INTEGRAND, V3 IS THE INCREMENT OF T.
800 H1=(S1+T1)*0.5-V3
810 REM-- Y1 I: THE PREVIOUS VALUE OF I1
820 I1=H1+Y1
830 t1=t1+1
840 T1=V3
850 S1=S1+V9
860 IF S1=A THEN 830
870 GOTO 730
880 I2=0
890 I2=0
900 J2=-1+PI+(1-T); D/2.4
910 IF J2<-1-14 THEN 970
920 S2=(R8-C4)+Z2zure(t2*D1+2)+1.5+EXP(J2)*(2+D)
930 H2=(S2+T2)*0.5+V3
910 T2=H2+Y2
920 Y2=I2
930 T2=S2
940 X=X+Y2
950 IF X>=-1 THEN Y=0
960 GOTO 870
970 Y3=6
980 J3=0
990 PRINT
1000 I:=A
1010 T3=0
1020 J3=1-P1+G2+D1-B1+4
1030 IF J3>14 THEN 1120
1040 S3=0.8+G2*2+H12+I12+1.5+K12*1.5+2+4
1050 H3=S3+T3+40.5+Y3
1060 J3=H3+Y3
1070 T3=T3+T3
1080 T3=T3
1090 S:=S+T3
1100 IF S>=6 THEN 1120
1110 GOTO 1020
1120 T:=I1+12+I3
1125 REM--THE VALUE OF F (CALCULATED ABOVE MUST BE ADDED
1129 REM--TO C4 TO GET F-T)
1130 PRINT "T EQUALS" T
1140 PRINT F: IF I2<12
1150 T=1+0.5
1160 IF T>2+B THEN 1180
1170 GOTO 690