MODELING THE AUSTENITE DECOMPOSITION INTO FERRITE AND BAINITE

By

FATEH FAZELI

B. Sc., Tehran University, 1990
M. Sc., Tehran University, 1995

A THESIS SUBMITTED IN PARTIAL FULLFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY in THE FACULTY OF GRADUATE STUDIES (Materials Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

February 2005

©Fateh Fazeli, 2005
ABSTRACT

Novel advanced high-strength steels such as dual-phase (DP) and transformation induced plasticity (TRIP) steels, are considered as promising materials for new generation of lightweight vehicles. The superior mechanical properties of these steels, compared to classical high strength steels, are associated with their complex microstructures. The desired phase configuration and morphology can only be achieved through well-controlled processing paths with rather tight processing windows. To implement such challenging processing stages into the current industrial facilities a significant amount of development efforts, in terms of mill trials, have to be performed. Alternatively, process models as predictive tools can be employed to aid the process development and also to design new steel grades. Knowledge-based process models are developed by virtue of the underlying physical phenomena occurring during the industrial processing and are validated with experimental data.

The goal of the present work is to develop an integrated microstructure model to adequately describe the kinetics of austenite decomposition into polygonal ferrite and bainite, such that for complex thermal paths simulating those of industrial practice, the final microstructure in advanced high strength steels can reasonably be predicted. This is in particular relevant to hot-rolled DP and TRIP steels, where the intercritical ferrite evolution due to its crucial influence on the onset and kinetics of the subsequent bainite formation, has to be quantified precisely. The calculated fraction, size and spatial carbon distribution of the intercritical austenite are employed as input to characterize adequately the kinetic of the bainite reaction. Pertinent to ferrite formation, a phenomenological, physically-based model was developed on the ground of the mixed-mode approach. The model deals with the growth stage since nucleation site saturation at prior austenite grain boundaries is likely to be attained during the industrial treatments. The thermodynamic boundary conditions for the kinetic model were assessed with respect to paraequilibrium. The potential interaction between the alloying atoms and the moving ferrite-austenite interface, referred to as solute drag effect, was accounted for rigorously in the model. To quantify the solute drag pressure the Purdy-Brechet approach was modified prior to its implementation into the model. The integrated model employs three main parameters, the intrinsic mobility of the ferrite-austenite interface,
the binding energy of the segregating solute to the interface and its diffusivity across the transformation interface. These parameters are clearly defined in terms of their physical meaning and the potential ranges of their values are well known. However, no direct characterization techniques are currently available to precisely measure them hence they are treated as adjustable parameters in the model. The model predicts successfully the overall kinetics of ferrite formation in a number of advanced steels.

The bainite evolution in different TRIP steels was analyzed using three available approaches, i.e. Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation, the Zener-Hillert formulation for diffusional growth and the displacive definition proposed by Bhadeshia. Overall, it turned out that the predictive capability of the three methodologies is similar. Further, some of the ensuing model parameters pertinent to each approach are difficult to interpret in terms of the underlying physics, which implies that all three models are employed in a semi-empirical manner.

Assuming diffusional transformation mechanism for bainite, the isothermal incubation time and the onset of bainite formation during continuous cooling treatments were described adequately. Consistently, for the purpose of process modeling, the diffusional description of bainite growth can potentially be employed. However, from an academic point of interest a more precise quantification for the nucleation part is still missing.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>xiii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>xvi</td>
</tr>
</tbody>
</table>

## Chapter 1: General Introduction

1.1 Advanced High-strength Steels.................. 1
1.2 Scope and Objective of the Thesis.................. 8

## Chapter 2: Austenite Decomposition into Ferrite

2.1 Literature Review.................................. 10
  2.1.1 Thermodynamics of phase transformation........... 10
    2.1.1.1 Orthoequilibrium.................................. 13
    2.1.1.2 Paraequilibrium.................................. 15
    2.1.1.3 Negligible partition local equilibrium.......... 16
  2.1.2 Austenite to ferrite transformation kinetics...... 18
    2.1.2.1 Nucleation......................................... 18
    2.1.2.2 Local equilibrium model for thickening of ferrite in Fe-C.......... 24
    2.1.2.3 Growth of ferrite in ternary and other multi-alloyed steels.......... 27
    2.1.2.4 Retarding effect of solute atoms.................. 31
    2.1.2.5 Mixed-mode model for ferrite growth.............. 35
    2.1.2.6 Overall kinetics of ferrite formation............ 36
  2.2 Model Development.................................. 39
    2.2.1 Characterizations of the thermodynamics of ferrite formation........... 39
      2.2.1.1 Paraequilibrium treatment.......................... 40
      2.2.1.2 Negligible partitioning local equilibrium boundaries.......... 44
    2.2.2 Modeling the growth kinetics of ferrite............ 45
      2.2.2.1 Carbon diffusion controlled model.................. 46
      2.2.2.2 Mixed-mode model.................................. 51
      2.2.2.3 Assessment of solute drag effect.................. 54
      2.2.2.4 Modification to Purdy-Brechet solute drag model............ 58
    2.2.3 Crucial parameters in the kinetic model............ 60
  2.3 Model Application.................................. 65
    2.3.1 Analysis of allotriomorph thickening in Fe-C alloys................. 65
      2.3.1.1 Prediction of carbon diffusion model.................. 66
      2.3.1.2 Prediction of mixed-mode model...................... 69
    2.3.2 Analysis of allotriomorph thickening in Fe-C-i systems.............. 76
      2.3.2.1 Comments on the experimental data.................... 76
      2.3.2.2 Suitable thermodynamic treatment of Fe-C-i alloys............. 79
Chapter 3: Bainite Transformation

3.1 Introduction

3.2 Literature Review

3.2.1 Overview

3.2.2 Mechanism of bainite transformation

3.2.3 Displacive mechanism of bainite transformation

3.2.4 Carbide precipitation

3.2.5 Thermodynamic criteria for displacive nucleation and growth

3.2.6 Displacive model to predict the overall kinetics of bainite

3.2.7 Diffusional theory of bainite formation

3.2.8 Mathematical expression for growth kinetics of a plate

3.2.9 Evaluation of bainite transformation kinetics

3.3 Study of Isothermal Bainite Formation in Fe-0.6C-1.5Mn-1.5Si

3.3.1 Experimental procedures

3.3.2 Experimental results

3.3.3 Modeling

3.3.3.1 Semi-empirical modeling approach

3.3.3.2 Modeling the incubation period

3.3.3.3 Diffusion model

3.3.3.4 Kinetic effect of strain energy in diffusion model

3.3.3.5 Displacive model

3.3.4 Summary and remarks (0.6C TRIP steel)

3.4 Study of Isothermal Bainite Formation in Fe-0.18C-1.55Mn-1.7Si

3.4.1 Experimental procedure and results

3.4.2 Modeling

3.5 Study of Continuous Cooling Bainite Formation in 0.19C-1.5Mn-1.6Si-0.2Mo TRIP Steel

3.5.1 Analyzing the onset of bainite reaction
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1-1</td>
<td>The annual production of typical structural materials [1]</td>
<td>1</td>
</tr>
<tr>
<td>Table 1-2</td>
<td>Car body components and their required properties [6]</td>
<td>3</td>
</tr>
<tr>
<td>Table 1-3</td>
<td>Typical mechanical properties of cold-rolled, high strength steels [7]</td>
<td>4</td>
</tr>
<tr>
<td>Table 2-1</td>
<td>Nominal values for n and m parameters [76]</td>
<td>37</td>
</tr>
<tr>
<td>Table 2-2</td>
<td>List of elements included in Fe2000 database in their maximum permitted level (wt%)</td>
<td>40</td>
</tr>
<tr>
<td>Table 2-3</td>
<td>Equilibrium austenite/ferrite transformation temperatures and ranges of measured transformation temperatures, $T_{meas}$, of the investigated ternary alloys</td>
<td>76</td>
</tr>
<tr>
<td>Table 2-4</td>
<td>The required values for the interface mobility (in terms of the ratio to Krielaart and van der Zwaag mobility, $M_{Fe-Mn}$) to replicate the measured thickening rate of Fe-0.12wt%C-3.3wt%Ni</td>
<td>83</td>
</tr>
<tr>
<td>Table 2-5</td>
<td>The required values for the interface mobility (in terms of the ratio to Krielaart and van der Zwaag mobility, $M_{Fe-Mn}$) to describe the overall kinetics of isothermal ferrite formation in Fe-0.17wt%C-0.74wt%Mn</td>
<td>97</td>
</tr>
<tr>
<td>Table 3-1</td>
<td>Reported values for adjustable parameters based on the best fit for Fe-C-Mn-Si alloys [23]</td>
<td>122</td>
</tr>
<tr>
<td>Table 3-2</td>
<td>Models of plate-lengthening rate [129]</td>
<td>129</td>
</tr>
<tr>
<td>Table 3-3</td>
<td>Maximum fraction of bainite measured experimentally using optical micrographs</td>
<td>137</td>
</tr>
<tr>
<td>Table 3-4</td>
<td>Parameters used in Equation 3.22 to predict the incubation period</td>
<td>145</td>
</tr>
<tr>
<td>Table 3-5</td>
<td>Values for adjustable parameters found for the 0.6C-1.5Mn-1.5Si steel in this work</td>
<td>154</td>
</tr>
<tr>
<td>Table 3-6</td>
<td>Growth rate of bainite plates for different transformation temperatures assessed using Zener-Hillert equation (0.41wt%C-1.55wt%Mn-1.7wt%Si austenite)</td>
<td>164</td>
</tr>
<tr>
<td>Table 3-7</td>
<td>Parameters used in displacive approach to describe the measured kinetics of bainite formation from an intercritically treated austenite with carbon content of 0.41wt%</td>
<td>165</td>
</tr>
<tr>
<td>Table 3-8</td>
<td>List of experimental treatments and the ensuing measurements of 0.16wt%C-1.5wt%Mn-1.6wt%Si-0.2wt%Mo, Mo-TRIP steel</td>
<td>168</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1-1 Schematic representation of the processing stages of DP and TRIP steels. ..... 5
Figure 1-2 Thermal and thermomechanical paths to produce TRIP steels. .......... 6
Figure 2-1 Free energy surfaces of γ and α and its equilibrium tie line for X₀. ........ 14
Figure 2-2 Iron reach corner, isothermal section of phase diagram for Fe-C-Mn at 700°C showing orthoequilibrium phase boundaries between ferrite and austenite, as well as the tie lines. ........................................... 14
Figure 2-3 Tangent planes to the free energy surfaces of α and γ in paraequilibrium condition. ................................................................. 16
Figure 2-4 Fe-C-Mn isotherm representing OE and NP-LE phase boundary [34]. ........ 17
Figure 2-5 The vertical section of a coherent pillbox nucleus [40]. ......................... 21
Figure 2-6 Carbon concentration profile along a direction perpendicular to the α/γ interface. ........................................................................ 25
Figure 2-7 Schematic illustration of the tetrakaidecahedron model for an austenite grain and the planar and the spherical geometry used in the diffusional model [51]. .......................................................................... 27
Figure 2-8 Schematic isothermal section of Fe-C-i system representing the interfacial concentration for ferrite growth under OE and NPLE conditions when the nominal composition of alloy is different. ....................... 28
Figure 2-9 The composition path of interfacial condition during isothermal growth [55]. ........................................................................... 30
Figure 2-10 Section of the free energy surfaces of ferrite and austenite along the concentration ray of carbon for a given Xᵢ/XᵢFe ratio. ........................................... 41
Figure 2-11 Isothermal section at 700°C for Fe-C-Mn system, (a) shows paraequilibrium and orthoequilibrium phase boundaries as well as OE tie lines, (b) shows the iron reach corner. .................................................. 43
Figure 2-12 Paraequilibrium pseudo-binary diagram illustrating the calculation of the chemical driving pressure at the start of ferrite growth where Xᵢ₀ = X₀. ................. 44
Figure 2-13 Isothermal section of phase diagram at 700°C for the Fe-C-Mn system comparing NPLE, PE and orthoequilibrium boundaries. ......................... 45
Figure 2-14 (a) Ferrite thin shell decorating austenite grain boundaries, ferrite formed partially at 735°C from austenite with grain size of 96μm in 0.17wt%C-0.74wt%Mn steel, followed by quenching to room temperature, (b) schematic representation of the ferrite growth as a spherical shell toward the center of austenite grain. ...................................................... 47
Figure 2-15 Node configuration for (a) planar and (b) spherical geometries. ............ 48
Figure 2-16 Carbon profile for various growth times calculated by diffusion model. Ferrite growth with planar geometry at 745°C from austenite of 50μm grain size in Fe-0.23wt%C was assumed. ....................................... 51
Figure 2-17 Carbon profile for various growth times calculated by the mixed-mode model for reaction at 745°C in Fe-0.23wt%C alloy assuming planar geometry and (a) M=0.05 μmol/J s and (b) M=0.38 μmol/J s. .................................................. 53
Figure 2-18 Chemical potential of solute in the α/γ interphase boundary [59]. ........ 55
Figure 2-19 Segregation profile inside the interface region (a) for various normalized velocities and $\Delta E=0$ and (b) for different values of $\Delta E$ for a stationary interface ($V=0$)..........................................................................................................................57

Figure 2-20 Comparison of the energy dissipated by solute drag for $E_o=1.5RT$ and $\Delta E=-4kJ/mol$, adopting the Purdy-Brechet model and the modified solute drag approach..........................................................................................................................59

Figure 2-21 Experimental parabolic rate constant in Fe-C alloys [92].................................................................................66

Figure 2-22 Zener predictions for parabolic rate constant and the measured [92] data in Fe-0.11wt%C..........................................................................................................................67

Figure 2-23 Comparison of the measured [92] parabolic rate constant with the prediction of the carbon diffusion model for (a) Fe-0.11wt%C, (b) Fe-0.22wt%C and (c) Fe-0.43wt%C alloys ..........................................................................................................................70

Figure 2-24 Measured allotriomorphs thickness and the predictions of mixed-mode model assuming $M_0=5.8$ and 1.27 cm mol/Js, as well as the calculation of the carbon diffusion model ($M_0=\infty$) for growth at 775°C in Fe-0.23wt%C..........................................................................................................................72

Figure 2-25 Experimental data [92] of parabolic rate constant and prediction of mixed-mode model assuming mobility of 5.8 and 0.75 cm mol/Js for (a) Fe-0.11wt%C, (b) Fe-0.22wt%C and (c) Fe-0.43wt%C alloys. The predictions of the diffusion model are included as well ..........................................................................................................................75

Figure 2-26 Experimental Measurements of parabolic growth rate constant of ferrite in C-Mn and C-Ni steels [34, 62].................................................................................77

Figure 2-27 The measured thickness of ferrite allotriomorph at different growth temperatures in Fe-0.12wt%C-3.3.wt%Ni alloy [94], the solid line represents linear regression..........................................................................................................................78

Figure 2-28 Predictions of the diffusion model using different thermodynamic conditions for ferrite thickening in (a) 1.52wt%Mn alloy at 730°C and (b) 3.3wt%Ni alloy at 665°C..........................................................................................................................80

Figure 2-29 Predictions of mixed-mode model and the experimental [94] growth of ferrite allotriomorphs for 0.12wt%C-3.3wt%Ni steel, intrinsic mobility is employed as the only fit parameter ..........................................................................................................................82

Figure 2-30 Arrhenius plot of fitted mobilities for 0.12wt%C-3.3wt%Ni resulting in an apparent activation energy of $-271kJ/mol$ shows mobility would have to be decreased with increasing temperature ..........................................................................................................................83

Figure 2-31 Effect of temperature on solute drag parameters to describe the experimental data [34] of ferrite plate thickening in Fe-0.21 wt pct C-1.52 wt pct Mn..........................................................................................................................85

Figure 2-32 Effect of the selection of the intrinsic mobility on solute drag parameters to describe the experimental data [59] of ferrite allotriomorph thickening in Fe-0.21 wt pct C-1.52 wt pct Mn..........................................................................................................................86

Figure 2-33 Solute drag parameters required to replicate the experimental growth kinetics [62] of ferrite at different temperatures in Fe-0.12wt%C-3.1wt%Mn..........................................................................................................................88

Figure 2-34 Required solute drag parameters to describe the growth kinetics of ferrite measured [62] at different temperatures in Fe-0.12wt%C-3.3wt%Ni..........................................................................................................................88
Figure 2-35 Variation of applied binding energy with temperature to describe the experimental growth rate of ferrite [34,62] in 0.12wt%C-3.1wt%Mn, 0.12wt%C-3.3wt%Ni and 0.21wt%C-1.52wt%Mn steels.................................89

Figure 2-36 Arrhenius plot for $D_b$ assuming constant values for the binding energy in Fe-0.12wt%C-3.1wt%Mn..................................................91

Figure 2-37 Arrhenius plot for $D_b$ assuming constant values for the binding energy in Fe-0.12wt%C-3.3wt%Ni.............................................92

Figure 2-38 Measured kinetics of isothermal ferrite formation in a 0.17wt%C-0.74wt%Mn steel with an austenite of grain size of 96μm..........................95

Figure 2-39 Measured and calculated ferrite fractions by optical metallography and the calculated ones assuming OE and PE.............................................95

Figure 2-40 Microstructure of Fe-0.17wt%C-0.74wt%Mn specimens reacted isothermally at (a) 735 and (b) 765°C, $d_γ=96μm$.................................................96

Figure 2-41 Experimental (symbols) and calculated (solid lines) kinetics of isothermal ferrite formation in the temperature range of 735 to 765°C in Fe-0.17wt%C-0.74wt%Mn with an initial austenite grain size of 96μm...............98

Figure 2-42 Variation of thermodynamic driving pressure and solute drag pressure with time for growth of ferrite at 735°C in 0.17wt%C-0.74wt%Mn steel (a) using modified SD model, (b) adopting the original Purdy-Brechet quantification.................................................100

Figure 2-43 Ferrite formation kinetics at 735°C in Fe-0.17 wt% C-0.74 wt%Mn showing the predictions adopting the original Purdy-Brechet solute drag theory and its modification, respectively..........................101

Figure 2-44 Measurements [63] and predictions for ferrite formation during continuous cooling from an initial austenite grain size of 18μm in 0.17wt%C-0.74wt%Mn steel.................................................................102

Figure 2-45 Measured [96] (symbols) and predicted (solid lines) kinetics of austenite decomposition into ferrite during continuous cooling of a dual-phase steel, Fe-0.06wt% C-1.85wt%Mn-0.16wt%Mo.....................................104

Figure 2-46 Comparison of observed data [97] and model prediction of ferrite formation kinetics during continuous cooling of TRIP steel, Fe-0.21C-1.53Mn-1.54Si(wt%), with an austenite grain diameter of 20μm .................105

Figure 2-47 Comparison of manganese diffusivity across ferrite-austenite interface for A36, DP and TRIP steels with bulk diffusivity in austenite, assuming 2δ of 1nm.................................................................106

Figure 2-48 Variation of manganese binding energy to α/γ interface with temperature for DP and TRIP steels.................................................................106

Figure 3-1 3D representation of lath and plate [109]. .......................................112

Figure 3-2 The $T_0$ line, (a) The free energy curves of austenite and ferrite and their relation to the different phase boundaries in the Fe-C diagram, (b) the relative location of $T_0$ in the Fe-C diagram [109].................................115

Figure 3-3 Evolution of three different bainite morphologies from the supersaturated plate [109].................................................................116

Figure 3-4 The change in volume fraction of bainite during austempering at different temperatures. Solid and dotted curves show calculated data based on the diffusional and displacive model, respectively [131].................................130
Figure 3-5 Schematic representation of the heat treatment cycle applied to isothermally form bainite at different temperatures from a single phase austenite featuring 13 and 40μm volumetric grain size.

Figure 3-6 Dilatometer responses recorded during isothermal bainite formation at different temperatures from austenite grain sizes of (a) 13μm and (b) 40μm.

Figure 3-7 TTT diagram of bainite formation from two different austenite grain sizes in Fe-0.6C-1.5Mn-1.5Si.

Figure 3-8 Optical micrographs showing bainite (dark gray phase) surrounded by martensite/austenite matrix formed at (a) 450, (b) 400 and (c) 350°C from dₐ=40μm.

Figure 3-9 SEM micrographs showing bainite surrounded by martensite/austenite matrix formed at different transformation temperatures from dₐ=40μm.

Figure 3-10 Incubation times of bainite formation as a function of temperature for different austenite grain sizes, i.e. 13 and 40μm.

Figure 3-11 Temperature dependency of the parameter b to provide optimal description of experimental data using the JMAK equation with n=1.

Figure 3-12 Comparison the experimental kinetics of isothermal bainite formation and model predictions adopting the JMAK equation.

Figure 3-13 Model prediction (lines) and experimental incubation period (points) of isothermal bainite formation from two prior austenite grain sizes, 13 and 40μm, in 0.6wt%C-1.5wt%Mn-1.5wt%Si steel.

Figure 3-14 Interfacial carbon concentration of austenite in equilibrium with ferrite plate bearing a tip curvature of ρ for different temperatures.

Figure 3-15 The variation of growth rate with the tip curvature of a ferrite plate for different reaction temperatures assuming the Zener-Hillert model.

Figure 3-16 Variation of the maximum growth rate of a bainite plate with ferrite-austenite interfacial energy, calculated for bainite formation at 400°C in 0.6wt%C-1.5wt%Mn-1.5wt%Si steel.

Figure 3-17 Comparison of the measured kinetics and the predictions of diffusion model for isothermal bainite formation in 0.6wt%C-1.5wt%Mn-1.5wt%Si steel.

Figure 3-18 Decreasing trend of the growth velocity of a plate as bainite fraction increases, transformation at 400°C in 0.6wt%C-1.5wt%Mn-1.5wt%Si steel.

Figure 3-19 Prediction (lines) of diffusion model modified with the effect of plastic work and the experimental kinetics (points) of bainite formation in Fe-0.6wt%C-1.5wt%Mn-1.5wt%Si alloy.

Figure 3-20 Displacive model predictions and the measured kinetics of bainite reaction for dₐ=40μm.

Figure 3-21 Comparison of the experimental data for the time of 50% transformed, t₅₀, and model predictions employing diffusion and displacive approaches.

Figure 3-22 Thermal cycle designed to form bainite from intercritically treated specimens with 0.18wt%C-1.55wt%Mn-1.7wt%Si initial composition.
Figure 3-23 Optical micrographs of intercritically treated samples transformed partially to bainite at 400 and 300°C. Ferrite matrix (white) estimated to be 58%, and the rest is a mixture of martensite (light gray) and packets of bainite (dark gray), 2% nital etched..........................159

Figure 3-24 SEM micrographs of intercritically treated samples transformed partially to bainite at 400 and 300°C.................................................................160

Figure 3-25 Kinetics of isothermal bainite evolution from intercritically treated samples featuring 42% austenite..............................................................161

Figure 3-26 Comparison of model prediction adopting JMAK approach and the experimental fraction of bainite formed after intercritical treatment in 0.18wt%C-1.55wt%Mn-1.7wt%Si steel..................................................163

Figure 3-27 Model prediction adopting diffusion approach and the experimental kinetics of isothermal bainite evolution from an intercritically treated austenite with carbon content of 0.41wt%.................................164

Figure 3-28 Comparison of the model prediction based on the displacive approach and the measured kinetic of isothermal bainite formation from an intercritically treated austenite with carbon content of 0.41wt% ......................166

Figure 3-29 Experimental data of overall austenite decomposition during continuous cooling treatments at 5°C/s after reheating at 950°C, ε=0 in 0.19wt%C-1.5wt%Mn-1.6wt%Si-0.2wt%Mo TRIP steel, (a) fraction transformed and (b) the rate of decomposition.............................................................169

Figure 3-30 Variation of the calculated driving pressure of bainitic ferrite formation at the transformation start temperature. The lower line shows G_N function [113], which is located about 300J/mol lower than the line followed by the data points.................................................................171

Figure 3-31 Normalized fraction of bainite formed during continuous cooling with CR=5°C/s for reheating at 950°C in Mo-TRIP steel..............................173

Figure 3-32 Variation of the maximum growth rate of a bainite plate with temperature and carbon concentration for Mo-TRIP steel........................174

Figure 3-33 Diffusion model prediction and the experimental kinetics of bainite formation for reheating at 1050°C and various subsequent treatments in Mo-TRIP steel.................................................................175

Figure 3-34 Comparison of the predicted (using the diffusion model) temperature for 50% transformation and the measured value for all the experiments listed in Table 3-8.................................................................177

Figure 3-35 Variation of the maximum growth rate with transformation temperature for different values of bainite fraction, i.e. different values of Gibbs free dissipation due to plastic work.................................................................178

Figure 3-36 Comparison of the predicted (using the diffusion model and accounting for the plastic work) temperature for 50% transformation and the measured value for all the experiments listed in Table 3-8.................................................................179
### LIST OF SYMBOLS

- \( a_L \): Lattice parameter
- \( \bar{a}_L \): Average lattice parameter of ferrite and austenite
- \( b \): Rate parameter in JMAK equation
- \( c_0 \): Initial carbon concentration of an alloy
- \( c_{eq} \): Equilibrium carbon concentration in phase \( j \)
- \( c_i \): Carbon concentration of node \( i \)
- \( c_i^j \): Carbon concentration of node \( i \) at time step \( j \)
- \( c_j^{nl} \): Interfacial carbon concentration in phase \( j \)
- \( c_{s,0} \): Initial concentration of substitutional component \( s \) in an alloy
- \( c_S(x) \): Concentration of segregating solute inside interface region
- \( d_y \): Austenite grain size
- \( f_i \): Volume fraction of phase \( i \)
- \( h^* \): Height of critical pillbox nucleus
- \( k \): Boltzmann's constant
- \( 2\ell \): Size of the remaining austenite grain
- \( 2\ell_0 \): Initial size of an austenite grain
- \( m \): Austenite grain size exponent
- \( n \): JMAK exponent
- \( n^* \): Number of atoms in contact with critical nucleus
- \( p \): Peclet number
- \( r^* \): Radius of the critical pillbox nucleus
- \( s \): Thickness of a ferrite allotriomorph
- \( u \): Size of a bainitic ferrite sub-unit
- \( v \): Velocity of ferrite-austenite interface
- \( v^B \): Growth velocity of a bainite plate
- \( v_{max}^B \): Maximum growth rate of a bainite plate
- \( x \): Length axis
- \( z \): Length axis
- \( z_i \): Geometrical factors depending on the assumed shape for critical nucleus
- \( A_i \): Parameters describing concentration and temperature dependency of \( \nu_{max}^a \)
- \( A_E \): Intercept of the linear temperature dependency of \( E_0 \)
- \( B_E \): Slope of the linear temperature dependency of \( E_0 \)
- \( C \): Normalized concentration of segregating solute
- \( C_1, C_2 \): Parameters used to describe the isothermal incubation time of bainite reaction
- \( D_0 \): Pre-exponential factor for solute diffusivity across interface
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_b$</td>
<td>Diffusivity of a segregating solute across transformation interface</td>
</tr>
<tr>
<td>$D_i^j$</td>
<td>Diffusivity of species $i$ in phase $j$</td>
</tr>
<tr>
<td>$E_o$</td>
<td>Solute-interface binding energy</td>
</tr>
<tr>
<td>$E(x)$</td>
<td>Interaction potential profile of solute inside interface</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>Chemical potential difference of the segregating solute across the interface</td>
</tr>
<tr>
<td>$G^j$</td>
<td>Molar Gibbs free energy of phase $j$</td>
</tr>
<tr>
<td>$G_{\text{critical}}$</td>
<td>Critical driving pressure required at the onset of bainite formation</td>
</tr>
<tr>
<td>$G_{\text{magnetic}}$</td>
<td>Magnetic contribution to Gibbs free energy of a phase</td>
</tr>
<tr>
<td>$G_N$</td>
<td>Universal nucleation function, criterion for displacive nucleation of bainite</td>
</tr>
<tr>
<td>$G_{\text{plastic}}$</td>
<td>Energy dissipation due to plastic accommodation of transformation strain</td>
</tr>
<tr>
<td>$\Delta G^*$</td>
<td>Activation energy for nucleation</td>
</tr>
<tr>
<td>$\Delta G_{\text{eff}}$</td>
<td>Effective driving pressure at ferrite-austenite interface</td>
</tr>
<tr>
<td>$\Delta G_{\text{int}}$</td>
<td>Thermodynamic driving pressure at ferrite-austenite interface</td>
</tr>
<tr>
<td>$\Delta G_{j\rightarrow k}$</td>
<td>Molar Gibbs energy change due to formation $k$ from phase $j$</td>
</tr>
<tr>
<td>$\Delta G_{\text{SD}}$</td>
<td>Energy dissipated by solute drag effect</td>
</tr>
<tr>
<td>$G_{\text{spike}}$</td>
<td>Energy dissipation due to solute diffusion inside a solute spike</td>
</tr>
<tr>
<td>$\Delta G_v$</td>
<td>Volumetric Gibbs energy change due to the formation of a new phase</td>
</tr>
<tr>
<td>$\Delta G_{y\rightarrow y'+\alpha}$</td>
<td>Free energy change for ferrite formation with paraequilibrium carbon content</td>
</tr>
<tr>
<td>$\Delta G_{y\rightarrow \alpha}$</td>
<td>Driving pressure for composition invariant transformation of austenite to supersaturated ferrite</td>
</tr>
<tr>
<td>$K_i$</td>
<td>Adjustable parameters relevant to the displacive model of bainite formation</td>
</tr>
<tr>
<td>$K_D$</td>
<td>Adjustable parameter to describe the overall kinetics of bainite formation by the diffusion model</td>
</tr>
<tr>
<td>$J_{\text{in}}, J_{\text{out}}$</td>
<td>Atomic flux of carbon to or from the interface</td>
</tr>
<tr>
<td>$\Delta J_{\text{net}}$</td>
<td>Net atomic flux of carbon across a moving ferrite-austenite interface</td>
</tr>
<tr>
<td>$M$</td>
<td>Intrinsic mobility of transformation interface</td>
</tr>
<tr>
<td>$M_e$</td>
<td>Pre-exponential factor for interface mobility</td>
</tr>
<tr>
<td>$N$</td>
<td>Density of viable atomic nucleation sites</td>
</tr>
<tr>
<td>$P_{\text{SD}}$</td>
<td>Solute drag pressure</td>
</tr>
<tr>
<td>$Q$</td>
<td>Activations energy for interface mobility</td>
</tr>
<tr>
<td>$Q_x$</td>
<td>Activation energy for the diffusivity of solute across interface</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
</tr>
<tr>
<td>$SC$</td>
<td>An imaginary component relevant to the substitutional sublattice in paraequilibrium</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>$T_{\text{S}}$</td>
<td>The highest temperature at which the displacive nucleation of bainite occurs</td>
</tr>
<tr>
<td>$V$</td>
<td>Normalized velocity of ferrite-austenite interface</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Molar volume</td>
</tr>
</tbody>
</table>
\( X \) Normalized distance inside ferrite-austenite interface
\( X_o \) Initial mole fraction of carbon in an alloy
\( X_C \) Mole fraction of carbon
\( X_{eq}^a, X_{eq}^r \) Equilibrium carbon mole fraction in ferrite or austenite
\( X_i \) Mole fraction of iron or substitutional elements
\( X_{i,o} \) Initial mole fraction of iron or substitutional elements in an alloy
\( X_{int}^j \) Interfacial mole fraction of carbon in phase \( j \)
\( X_{i,k} \) Mole fraction of iron or substitutional elements in specific location \( k \)
\( X_{pE}^a, X_{pE}^r \) Paraequilibrium mole fraction of carbon in ferrite or austenite
\( X_{pE}^r \) Carbon content at the austenite side of the bainitic ferrite-austenite interface corrected by capillary effect
\( Y_i \) Site fraction of species \( i \) (in a sub-lattice)
\( Z \) Zeldovich nonequilibrium factor
\( \alpha \) Ferrite
\( \beta^* \) Nucleation frequency factor
\( \delta \) Half thickness of interface
\( \gamma \) Austenite
\( \gamma_B \) Shear component of transformation strain associated with bainite formation
\( \gamma_i \) Activity coefficient of component \( i \)
\( \varepsilon_i^i \) Wagner’s interaction coefficient
\( \theta_B \) Maximum fraction of bainite determined experimentally
\( \theta_i \) Ratio of substitutional mole fraction to iron mole fraction
\( \gamma \) Chemical potential of \( i \) in standard state
\( \mu_i \) Chemical potential of \( i \) in phase \( j \)
\( \Delta \mu_i^{j\rightarrow k} \) Change in the chemical potential of \( i \) during phase change \( j \rightarrow k \)
\( \mu_{SC}^j \) Chemical potential of an imaginary substitutional component \( SC \) in phase \( j \) relevant to paraequilibrium pseudo-binary section
\( \rho \) Tip curvature of a bainite plate
\( \rho_C \) Critical tip curvature of a plate
\( \sigma_{ar} \) Interfacial energy between ferrite and austenite
\( \sigma_{yr} \) Interfacial energy for austenite grain boundaries
\( \tau \) Incubation time
\( \tau_m \) Ratio of temperature to Curie temperature
\( \tau_y \) Yield strength of austenite
\( \omega \) Driving pressure exponent in Russell’s equation
\( \Omega_o \) Supersaturation in front of a bainite plate
ACKNOWLEDGMENT

It was a great opportunity for me to pursue my Ph.D. at UBC, in a research group conducted by decent and talented scientists, “Praise be to God, who has guided us to this”.

I am forever indebted to my supervisor Dr. Matthias Militzer for his efficient guidance, professional support and constant encouragement throughout the course of this work. This provided me the enthusiasm to efficiently overcome the challenges.

A sincere appreciation is extended to Dr. Warren Poole for his constructive advices. I have been fortunate to benefit of his expertise in various aspects of this research.

Special thanks to all the colleagues and officemates for providing a friendly environment that I was always pleased to work in. Financial support from the Natural Science and Engineering Research Council of Canada, and also the Stelco Fellowship are gratefully acknowledged.

The great sacrifice, wisdom and patience of my wife are much appreciated. This thesis is dedicated to my precious parents.
Chapter 1: General Introduction

1.1 Advanced High-strength Steels

Among structural materials, steel is of the leading production tonnage globally. As indicated in Table 1-1 it exceeds 960 million tones in 2003 [1], about 60% of which is made from recycled scrap. Further, compared to other metallic alloys, its production requires lower amount of energy. This substantially contributes in maintaining a sound ecology. There is virtually no limit in alloying strategies and there are currently more than 3500 different steel grades available. The full potential of this extensive diversity in chemistry, and consequently numerous distinctive transformation behaviors, can be exploited by applying appropriate thermomechanical treatments, such that various phase configurations and morphologies are likely to evolve in practice. The enormous multiplicity in the microstructures of steel results in diverse combination of mechanical properties which are suitable for a wide range of applications.

Table 1-1 The annual production of typical structural materials [1]

<table>
<thead>
<tr>
<th>Material</th>
<th>Production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>960 million tons (2003)</td>
</tr>
<tr>
<td>Aluminum</td>
<td>21 million tons (2002)</td>
</tr>
<tr>
<td>Copper</td>
<td>14.9 million tons (2002)</td>
</tr>
<tr>
<td>Portland cement</td>
<td>87.8 million tons (2000)</td>
</tr>
<tr>
<td>Timber</td>
<td>300 million m$^3$ (2001)</td>
</tr>
</tbody>
</table>

Despite many financial crises that infrastructural industries have been facing, steel production is still a profitable, active and dynamic industry. A proof to this argument is the fact that 75% of the current steel grades have been developed in the past 20 years and in particular, 70% of the steels used in automotive applications today did not exist 10 years ago.
[1]. This also implies that much progress in composition and processing of new steels were driven by the automotive industry which requires the most demanding functionality of steels for vehicle components and bodies [2,3,4]. However, in order to improve fuel efficiency and reduce emission, special efforts were made to reduce vehicle weight not only by optimizing the body design but also in part by introducing plastic parts and employing light metals. For instance the weight fraction of steel being used in a family car was decreased from 74% in 1978 to 67% in 1997. However, over the same period the incorporation of high strength steels was increased from 4% to 9%, a rise that is unique compared to the growth of any other material class in automotive applications [5].

Several groups of cold- and hot-rolled, high strength steels have been developed to satisfy the aforementioned demand for automotive applications. Although weight reduction would be possible through using stronger materials, there is a common trend that the ductility deteriorates as strength increases. Depending on the function of individual components, the required properties vary in detail, as summarized in Table 1-2 [6]. Examples of typical mechanical properties of commonly used cold-rolled formable steels are presented in Table 1-3 [7].

High Strength Low Alloy (HSLA) steels were developed by combining the benefits of precipitation hardening of microalloying elements with the advantages of grain refinement. Controlled rolling and accelerated controlled cooling are the two common processing routes of HSLA steels [8]. A complex chemistry plus complicated thermomechanical processing have led to the introduction of the most advanced steel in this class, X100 grade steels with a tensile strength of more than 800MPa for pipeline applications [9]. The main disadvantages
of HSLA steels are their inferior formability and high deformation resistance during hot or cold rolling.

Interstitial Free (IF) steels have a carbon and nitrogen content of 20-40 ppm, which is removed from solution by adding Ti/Nb as carbide and nitride formers. These steels are the current choice for the most complex parts of car bodies because of their high r-value and superior formability. However the upper limit of yield and tensile strength in IF steels is about 320 and 450MPa, respectively [10].

**Table 1-2 Car body components and their required properties [6].**

<table>
<thead>
<tr>
<th>Components</th>
<th>Required properties</th>
<th>Factors for thickness selection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Body panels</td>
<td>Deep drawability, stretchability, shape flexability, panel stiffness, dent resistance, corrosion resistance</td>
<td>Panel stiffness, dent resistance</td>
</tr>
<tr>
<td>Structural members</td>
<td>Stretchability, bendability, shape flexability, structural rigidity, crashworthiness, fatigue strength, corrosion resistance, weldability</td>
<td>Structural rigidity, crashworthiness, fatigue strength</td>
</tr>
<tr>
<td>Undercarriage parts</td>
<td>Stretchability, stretch flanging, shape flexability, structural rigidity, crashworthiness, fatigue strength, corrosion resistance, weldability</td>
<td>Structural rigidity, fatigue strength</td>
</tr>
<tr>
<td>Reinforcements</td>
<td>Bendability, shape flexability, crashworthiness, weldability</td>
<td>Crashworthiness</td>
</tr>
</tbody>
</table>

Bake Hardenable (BH) ultra-low carbon steels where a few ppm carbon remain in solution are suitable for outer large panels. They offer high formability and high dent resistance simultaneously. Hardening occurs during the paint baking process and results in a strength
increase of approximately 40MPa. This is indeed a strain aging process and aids the material to be potentially dent resistant.

Table 1-3 Typical mechanical properties of cold-rolled, high strength steels [7].

<table>
<thead>
<tr>
<th>Steels</th>
<th>Yield strength (MPa)</th>
<th>UTS (MPa)</th>
<th>El. (%)</th>
<th>r-value</th>
<th>n-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microalloyed</td>
<td>320</td>
<td>440</td>
<td>28</td>
<td>1.3</td>
<td>0.17</td>
</tr>
<tr>
<td>Bake Hardening</td>
<td>210</td>
<td>320</td>
<td>40</td>
<td>1.6</td>
<td>0.22</td>
</tr>
<tr>
<td>Interstitial Free</td>
<td>220</td>
<td>390</td>
<td>37</td>
<td>1.9</td>
<td>0.21</td>
</tr>
<tr>
<td>Dual Phase</td>
<td>350</td>
<td>600</td>
<td>27</td>
<td>0.9</td>
<td>-</td>
</tr>
<tr>
<td>TRIP</td>
<td>400</td>
<td>640</td>
<td>32</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Super-ultralow Carbon</td>
<td>200</td>
<td>300</td>
<td>45</td>
<td>2.0</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Dual phase (DP) and transformation induced plasticity (TRIP) steels have been proposed as new materials for more demanding applications in the automotive industry. These steels are characterized by complex multiphase microstructures that provide an excellent combination of strength and formability. Both DP and TRIP steels are processed in the intercritical region either by cooling from the austenite region after hot rolling or by annealing after cold rolling. The goal of this processing step is to form an austenite-ferrite mixture with a ferrite fraction as desired in the final microstructure. DP steels are then quickly cooled to room temperature such that the remaining austenite transforms to martensite whereas the situation is more complex for TRIP steels, as illustrated schematically in Figure 1-1.

Dual phase steels with a ferrite-martensite microstructure represent an improved combination of strength and formability [11,12]. The Ultra Light Steel Auto Body (ULSAB) project suggested that by employing different grades of DP steel (about 75% by weight) in the proposed advanced vehicle concept a total weight reduction of 25% could be attained [3].
General Introduction

The conventional chemistry range of these DP steels is: 0.04-0.2 C, 1-1.5Mn and 0.2-0.4Si (wt%). In general, cold-rolled DP steels are directly quenched to room temperature after intercritical annealing in ferrite+austenite region, such that the formation of pearlite or bainite is suppressed [13]. The resulting ferrite-martensite structure provides attractive properties such as: absence of stretcher strain, low yield/tensile strength ratio of about 0.5, and an initial high work hardening rate that warrants good formability. The low yield point has been attributed to the presence of mobile dislocations in the ferrite matrix around the martensite islands [14,15]. Finely dispersed martensite, which acts as obstacles for further dislocation motion, interacts severely with dislocations resulting in a high work hardening rate. The tensile strength of DP steels is primarily controlled by martensite volume fraction in the structure.

Figure 1-1 Schematic representation of the processing stages of DP and TRIP steels.

Adding more silicon or other alloying elements, which prevent carbide formation, to DP steel chemistries, about 1-2%, and introducing a bainite formation step after intercritical treatment as shown in Figure 1-1, a substantial amount of austenite can be retained in the final structure [16,17,18]. Indeed, during partial bainite formation, austenite is further enriched with carbon such that it can be stabilized to room temperature, i.e. upon subsequent cooling the
transformation to martensite is unlikely to take place. The metastable austenite transforms to martensite during later deformation, e.g. in a stamping operation, thereby leading to the TRIP effect. The volume expansion associated with transformation results in a localized increase of strain hardening during straining [15]. This postpones the onset of necking that finally leads to very high uniform elongation and a superior formability index (UTS × El%). Moreover, the resulting martensite can also contribute to further strengthening the material.

These TRIP-assisted multiphase steels are richer in alloying elements than conventional DP steels, i.e.: 0.15-0.4C, 1-2Mn and 1-2Si (wt%) [10]. The two following principal ways have been proposed to develop TRIP multiphase steels, which are depicted in Figure 1-2: (i) Controlled rolling during hot rolling to obtain hot-rolled TRIP, (ii) The combination of intercritical annealing and isothermal holding in the bainitic reaction region, results in cold-rolled TRIP steels. Due to high content of Si in traditional TRIP steels to suppress carbide formation, the wettability of the surface during the subsequent hot-galvanizing treatment is drastically degraded. This drawback triggered the development of a new generation of TRIP steels in which Si is partially or totally replaced by other elements such as Al or P [19].

*Figure 1-2 Thermal and thermomechanical paths to produce TRIP steels.*
General Introduction

The design and development of the aforementioned high-strength steels have been accomplished by considering the physical metallurgy concepts that dictate the microstructure evolution in response to the processing route the steel is exposed to. A crucial stage in processing these advanced high strength steels is the austenite decomposition into ferrite and other, non-equilibrium transformation products. These transformations primarily take place on the run out table of hot strip mills and/or occur during intercritical annealing treatments. Therefore, to obtain a final microstructure of the required features in terms of phase fraction, morphology and distribution, the appropriate control of the austenite decomposition kinetics is crucial. Consequently, microstructure models have gained significant attention as predictive tools to optimize the processing parameters to aid the design of novel steel grades.

An example of these sophisticated microstructure models that have been implemented into the steel industry as a predictive tool, is the Hot Strip Mill Model (HSMM)[20], developed at UBC. Here, to describe the transformation kinetics a semi-empirical approach is employed using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation together with additivity rule [21]. Although the JMAK approach is a versatile modeling tool to describe the kinetics of various transformation products, due to its entirely empirical nature it cannot provide any information regarding transformation mechanism. As a further limitation of this approach, the validity of the adjustable parameters determined from experimental data, is confined to the cases that already have been examined in the laboratory. It is thus imperative to develop a more physically-based model that gives insight into the actual mechanism of austenite decomposition. This constitutes the main motivation behind the present research and will thoroughly be discussed in the following chapters.
1.2 Scope and Objective of the Thesis

1. The overall objective of the present work is to develop a thorough model to describe precisely the microstructural evolution during austenite decomposition into ferrite and bainite, relevant to industrial processing of hot-rolled advanced high-strength steels, such as DP and TRIP products. As a unique feature, all components of the proposed model will be developed on a solid physical foundation such that the theoretical knowledge are integrated elegantly into an efficient predictive tool applicable to real industrial processing. Although some of the individual model components had already been developed, they suffer from some conceptual flaws and artifacts that have to be first identified and corrected. Further, the novelty of the present model development is the adequate couplings of these model components and their application to complex cooling paths and steel chemistries.

2. Relevant to ferrite formation, the goal of the first part of this research is to develop a phenomenological physically-based model for the ferrite growth kinetics such that both thermodynamic and kinetic effects of alloying elements are explicitly taken into account. The model is designed to describe non-isothermal ferrite formation under industrial processing conditions during which the reaction features early stage nucleation site saturation, polygonal morphology for the growing phase, and a rather fast growth rate preventing partitioning of substitutional elements.

3. Regarding subsequent austenite decomposition into bainite, the second part of the present research is devoted to experimental and theoretical characterization of bainite evolution in materials featuring a composition similar to those adopted traditionally for TRIP steels. Available modeling approaches, e.g. diffusional [22] and displacive
[23], are examined and their predictive capabilities are identified. One of the goals of this section is also to define a potential criterion for transition from ferrite to bainite formation during continuous cooling treatments.

Although the proposed approach is aimed to provide an overall austenite decomposition model that integrates ferrite and bainite formations, different modeling strategies are adopted for each transformation. Therefore they will be discussed in two separate chapters. The thesis is organized as follows. Following the introduction, a brief literature review relevant to ferrite formation constitutes the first part of the second chapter. Then the model development for ferrite is delineated. Next the experimental kinetics and its analysis using the proposed model is presented. The third chapter deals with the bainite reaction. Here, following the outline of the relevant literature, available modeling approaches are examined. In the last chapter, conclusions and recommendations are given for the overall austenite decomposition modeling.
Chapter 2 : Austenite Decomposition into Ferrite

2.1 Literature Review

2.1.1 Thermodynamics of phase transformation

Characterization the thermodynamics of a transformation is the first essential step in modeling the kinetics of a reaction. Concerning the austenite decomposition to ferrite, thermodynamics provides information about ferrite-austenite phase boundaries and the driving pressure for the reaction. This is accomplished by modeling the composition- and temperature-dependence of the Gibbs free energy of both phases and subsequently by quantifying the chemical potential of individual components in austenite and ferrite phases. Since the steels under investigation usually contain more than one alloying element, the interaction among individual components in solution has to be addressed adequately in the thermodynamic model.

The mathematical description of the Gibbs energy can be formulated in the framework of the regular solution model in which the chemical potential of species $i$ is of the following form:

$$
\mu_i = \mu_i^0 + RT \ln X_i + RT \ln \gamma_i
$$

(2.1)

where $\mu_i^0$ represents the standard energy of the pure element $i$, $X_i$ and $\gamma_i$ denote the mole fraction and activity coefficient of component $i$, respectively, and $RT$ has its usual meaning. The second term is related to the entropy assuming random mixing and the last part is included to show the deviation from ideality and normally is referred to as partial excess term.
The activity coefficient, $\gamma$, in multicomponent systems accounts for the interaction among the different species. Usually, Wagner’s interaction coefficients are employed which are defined as:

$$
\varepsilon_i^j = \frac{\partial \ln \gamma_i}{\partial X_j}
$$

(2-2)

Using Taylor’s expansion for $\ln \gamma$ and adopting a standard state at infinite dilution for all the alloying additions, the appropriate expression for iron and solutes in either ferrite or austenite phases can be derived [24]:

$$
\ln \gamma_{Fe} = -\frac{1}{2} \sum_{i=C,Mn,...} \varepsilon_i^{Fe} X_{Fe} X_i
$$

(2-3)

$$
\ln \gamma_k = \sum_{i=C,Mn,...} \varepsilon_k^i X_i \quad (\text{for } k=C, Mn, ...)
$$

(2-4)

where $X_{Fe}$ and $X_i$ are the mole fraction of iron and the alloying element, respectively. This constitutes the thermodynamic model based on which Kirkaldy and coworkers [25] developed a method to predict the phase equilibria in alloyed steels. It has to be noted that due to the lack of experimental data, only the binary interaction is considered.

In many cases the size, shape and electronegativity of the constituents are not similar and the assumption of random mixing is no longer valid. For instance, carbon occupies the interstitial lattice sites in ferrite and austenite, respectively. Thus, it is more realistic to consider two sublattices, i.e. interstitial and substitutional ones. The concept of the regular sublattice model for ionic metals and interstitial solutions was first proposed by Hillert and Staffansson [26]. Their analysis dealt with the pair-wise mixing of four components in two sublattices. In this approach iron and all the other substitutional atoms occupy one sublattice while carbon and vacant interstitials reside in the second sublattice. Further to express the concentration the site fraction is used instead of mole fraction bearing in mind that ferrite has three
interstitial sites per metal atom whereas austenite has only one. Then the site fraction for substitutional, \( Y_i \), and carbon, \( Y_c \), atoms is defined as:

\[
Y_i = \frac{X_i}{1 - X_c} \quad \text{(for i=Fe, Mn,...)} \tag{2-5}
\]

\[
Y_c = \eta \frac{X_c}{1 - X_c} \tag{2-6}
\]

where \( \eta \) is 1 for austenite and 3 for ferrite considering octahedral interstitial sites. The description of the Gibbs energy applicable to either ferrite or austenite containing only carbon and one alloying element is given in Appendix I.

The theory of regular sublattice was later extended to systems of several sublattices and components by Sundman and Ågren [27] with the goal of developing a practical numerical recipe, which can be implemented easily into a computational thermodynamic software. The frequently used Thermo-Calc software employs this numerical procedure together with Gibbs energy minimization technique [28] to assess the phase equilibria in complex, multicomponents systems.

It is worth to note that in case of ferro-magnetism, i.e. for the ferrite phase, the magnetic contribution has to be accounted for in the mathematical description of the Gibbs energy. The detailed analysis of the magnetic effect by Hillert and Jarl [29] led to the following quantification for this extra term:

\[
G_{\text{magnetic}} = RT g(\tau_m) \ln(\beta_m + 1) \tag{2-7}
\]

where \( \tau_m = T / T_C \) and \( T_C \) is the Curie temperature which is composition dependent and \( \beta_m \) is the magnetic momentum. The function \( g(\tau_m) \) takes different forms above and below the Curie temperature (cf. Appendix I).
2.1 Literature Review

In ternary Fe-C-i alloys and multi-alloyed steels containing one or more substitutional elements ferrite formation hardly occurs under complete equilibrium condition. This equilibrium state is referred to as so-called orthoequilibrium and can only be achieved in the whole system after sufficiently long time [30]. Therefore, due to kinetic restrictions the system is likely to adopt different meta-equilibrium states depending on partitioning behavior of alloying elements during austenite decomposition. Paraequilibrium (PE) [31, 32] and negligible partition local equilibrium (NPLE) [32,33,34] are the two main alternative descriptions that can be assumed to assess the thermodynamics of the reaction to be examined. It has to be noted that these two states tend to establish at the migrating ferrite-austenite interface while orthoequilibrium implies a full equilibrium state in the whole system [30]. We shall now provide a brief comment on these thermodynamic conditions.

2.1.1.1 Orthoequilibrium

Orthoequilibrium is established when all the components partition completely between the parent and product phases. The orthoequilibrium phase boundaries are the locus of equilibrium tie lines for various temperatures. A tie line connects two points between parent and product phases, for instance austenite and ferrite, respectively, at which the chemical potentials of each component in both phases are identical, i.e. [35]:

$$\mu_i^e = \mu_i^f \quad \text{(for } i=Fe, C, Mn, ... \text{)}$$  \hspace{1cm} (2-8)

In binary alloys, the tie line is the common tangent to the free energy curves. In a ternary system the tie line is located on the common tangent plane to the free energy surfaces and includes the projection of alloy composition, $X_0$, as depicted in Figure 2-1 for the Fe-C-Mn system. The lever rule can be applied to the tie line to assess the fraction of each phase.
For a range of alloy compositions, the projection of various tie lines on the composition triangle, which defines the two-phase field region at a given temperature, is usually represented by a perpendicular-axis plot of element A versus B, as illustrated in Figure 2-2 for the Fe-C-Mn system at 700°C.

Figure 2-2 Iron reach corner, isothermal section of phase diagram for Fe-C-Mn at 700°C showing orthoequilibrium phase boundaries between ferrite and austenite, as well as the tie lines.
2.1 Literature Review

2.1.1.2 Paraequilibrium

During the conventional thermal treatment of steels, transformation time is not sufficient to let the complete partitioning of all components take place, i.e. the system cannot approach orthoequilibrium. However, for more mobile diffusing species, e.g. carbon, partitioning is kinetically possible. Paraequilibrium depicts the equilibrium state where only interstitial atoms are free to redistribute while the substitutional sublattice remains configurationally frozen during the transformation. Then the ratio of mole fraction $X_i/X_{Fe}$ for each substitutional alloying elements $i$ is the same in ferrite and austenite, respectively, and is given by its nominal bulk value:

$$\frac{X_{i,o}}{X_{Fe,o}} = \frac{X_{i}^{a}}{X_{Fe}^{a}} = \frac{X_{i}^{f}}{X_{Fe}^{f}} = \theta_i$$  \hspace{1cm} (2-9)

In contrast to carbon, the chemical potential of substitutional atoms cannot be equal in ferrite and austenite, although the following expression can be derived in paraequilibrium conditions for substitutional elements:

$$\Delta \mu_{Fe}^{r->a} + \sum_i \theta_i \Delta \mu_i^{r->a} = 0$$  \hspace{1cm} (2-10)

whereas for carbon:

$$\mu_{c}^{a} = \mu_{c}^{f}$$  \hspace{1cm} (2-11)

holds. Here, $\mu_{c}^{a}$ and $\mu_{c}^{f}$ are the chemical potentials of carbon in ferrite and austenite, respectively, whereas $\Delta \mu_{Fe}^{r->a}$ and $\Delta \mu_i^{r->a}$ denote the chemical potential difference between austenite and ferrite phases for Fe and substitutional elements $i$, respectively.

In a ternary system, the above constraints imply that the tie lines have to be composition rays of the mobile species carbon [31]. This tie line is not identical to the orthoequilibrium tie line and does not fall on the common tangent plane to the two free energy surfaces. However, the
2.1 Literature Review

The tie line is situated on the common tangent line to the free energy surfaces of ferrite and austenite, which defines the carbon concentration in each phases, i.e. $X_{PE}^\alpha$ and $X_{PE}^\gamma$ as shown in Figure 2-3. Along the component ray the mole fraction of any component $j$ can be found as a function of carbon content based on the following mass balance equation:

$$\frac{X_j}{\theta_j}(1 + \sum_{i=1}^n \theta_i) + X_C = 1$$

(2-12)

The tie line in paraequilibrium is actually the intersection of two tangent planes, one to the free energy surface of ferrite at $X_{PE}^\alpha$ and the other to the free energy surface of austenite at $X_{PE}^\gamma$. Looking at the geometry of this configuration, as shown in Figure 2-3, it is evident that conditions expressed by the above equations are satisfied.

![Figure 2-3 Tangent planes to the free energy surfaces of α and γ in paraequilibrium condition.](image)

2.1.1.3 Negligible partition local equilibrium

Ortho- and paraequilibrium describe the two extremes regarding the partitioning of substitutional elements. The intermediate state can be defined when local redistribution at
migrating ferrite-austenite interface tends to occur. The boundary of negligible partition local equilibrium (NPLE) divides ternary isotherm into the two region of low and high supersaturation [34]. In the latter region, slow-diffusing solute, e.g. Mn, can only redistribute locally at the interface resulting in a solute spike. The bulk concentration of this element remains unchanged. However, the interfacial activity of carbon is determined by this spike. Regarding NPLE condition, as also illustrated in Figure 2-4, it is assumed that manganese bulk concentration of ferrite and austenite are the same as its concentration in the initial alloy, i.e. they all fall on the Mn isoconcentration line [34]:

\[ X_{Mn,o} = X_{Mn,bulk}^{a} = X_{Mn,bulk}^{p} \]  \hspace{1cm} (2-13)

![Figure 2-4 Fe-C-Mn isotherm representing OE and NP-LE phase boundary [34].](image)

Therefore the carbon and manganese contents of the interface at the ferrite side can be found simply. Further, local equilibrium of Mn at the interface necessitates that:

\[ \mu_{Mn, int}^{a} \left( at \ X_{Mn} = X_{Mn,bulk}^{a} \right) = \mu_{Mn, int}^{p} \left( at \ X_{Mn} = X_{Mn, int}^{p} \right) \]  \hspace{1cm} (2-14)
The above equation gives point OE, i.e. the interfacial manganese concentration at the peak of the Mn spike, which governs the activity of carbon at the interface, such that the intersection of the carbon isoactivity line with Mn isoconcentration line determines the interfacial carbon concentration at the root of the manganese spike, i.e. point NPLE.

2.1.2 Austenite to ferrite transformation kinetics

2.1.2.1 Nucleation

The formation of a new phase is initiated by nucleation, where due to thermal fluctuation of atoms a number of clusters in form of the new phase emerge inside the parent phase, preferentially at heterogeneous sites. In general, these clusters are not necessarily of the equilibrium crystal structure and composition of the product phase and nucleation can primarily be facilitated by formation of metastable lattices. However, in case of ferrite nucleation no transition metastable phases have been observed. Those clusters that are larger than a critical size provide stable nuclei. Tracking the evolution of nuclei and characterization of their structure, in particular the interface as well as the shape, are a challenging task for available experimental techniques due to the very tiny scale of a nucleus, e.g. about 10 to 1000 atoms. This constitutes a major challenge for the study of nucleation phenomena and modeling its kinetics. However, the recent emergence of X-ray synchrotrons capable of 3D data analysis and high energy neutron beams promises in-situ probing of dynamic and meso-scale atomic phenomena, such as nucleation in the solid state [36]. The pioneering attempt to characterize the nucleation of individual grains using these new facilities by Offerman et al.[36] provides new insight into this challenging area, yet more
mature software to interpret the raw data and finer time resolution of data acquisition are required.

Lacking intragranular inoculants, e.g. intermetallic inclusion, shear bands and subgrain boundaries, ferrite nucleates heterogeneously on potential sites, i.e. austenite grain corners, grain edges and grain faces, respectively [37]. To minimize the interfacial energy a semi coherent ferrite-austenite interface tends to appear giving rise to preferred orientation relationships between parent austenite and ferrite nuclei, e.g. \{111\}_\gamma/\{110\}_\alpha. Enomoto et al. [38] compared nucleation rates calculated for grain edges and faces with experimental data in binary and ternary Fe-C alloys and found that only at very low undercooling does nucleation on edges dominate. Therefore, the total nucleation rate correlates with faces for most transformation temperatures. They also showed that the amount of undercooling at which face nucleation becomes predominant depends on prior austenite grain size. At smaller grain size, the temperature range in which edge nucleation dominates should be larger. As the austenite grain size decreases, the ratio of the grain edges length to the grain faces area per unit volume of austenite increases, this leads to higher probability of nucleation at grain edges.

The nucleation rate of ferrite at the austenite grain boundaries can be expressed by the classical nucleation theory, i.e.:

\[
\dot{N} = N \beta^* Z \exp(-\frac{\Delta G^*}{kT}) \exp(-\frac{\tau}{l})
\]

where \(N\) is the density of viable atomic nucleation sites, the frequency factor \(\beta^*\) is the rate at which single atoms are added to the critical nucleus, \(Z\) is the Zeldovich nonequilibrium factor, \(\Delta G^*\) is the activation energy for critical nucleus formation and \(\tau\) is the incubation
2.1 Literature Review

The time-independent portion of this equation is referred to as the steady state nucleation rate, \( I_s \), when \( t \ll \tau \).

To apply classical nucleation theory to ferrite nucleation, the shape of the critical nucleus should be determined. This shape has a pronounced effect on the calculated nucleation rate, thus the selected model should provide consistent results with experimental values.

If the interphase boundary is assumed to be incoherent featuring isotropic interfacial energy, then the interface is likely to be evenly curved such that the critical nucleus tends to form at grain faces in the shape of two spherical caps. Following the same argument, the newly formed particle at grain edges would be bounded by three equivalent spherical surfaces with similar dihedral angles. At grain corners the nucleus would be encompassed by four such spherical surfaces. The geometries, in particular the spherical cap shape, were frequently used in early studies to analyze the nucleation kinetics. For instance, adopting the aforementioned models for the critical nucleus with incoherent interfaces, Clemm and Fisher [39] performed a detailed theoretical analysis regarding nucleation at austenite grain boundaries, which yielded the following expression for the activation energy, \( \Delta G^* \):

\[
\Delta G^* = \frac{4}{27} \frac{(z_2 \sigma_{\alpha \gamma} - z_1 \sigma_{\gamma \gamma})^3}{z_3 \Delta G_v^2}
\]  

(2-16)

where \( \sigma_{\alpha \gamma} \) and \( \sigma_{\gamma \gamma} \) denote interfacial energy for interphase and grain boundaries, respectively, \( z_1, z_2 \) and \( z_3 \) are the factors to be determined from the assumed geometry and the value considered for the ratio of \( \sigma_{\alpha \gamma} / \sigma_{\gamma \gamma} \), and \( \Delta G_v \) represents the volumetric Gibbs energy change for ferrite formation. For grain face nucleation the value reported for the geometrical factors \( z_1, z_2 \) and \( z_3 \), are 3.7, 1.6 and 0.48, respectively, when the ratio of \( \sigma_{\alpha \gamma} / \sigma_{\gamma \gamma} = 0.7 \) was assumed.
2.1 Literature Review

Although the spherical cap model can be treated easily and assumes only a single interfacial energy for the entire ferrite-austenite interface, the classical nucleation theory assuming this nucleus shape fails to describe the experimental nucleation rates [36,40]. Therefore some modification, in terms of the geometry and the coherency of the embedded surfaces have been discussed.

Among the efforts to quantify the nucleation rate, the measurement carried out by Lange et al. [40] offered a thorough series of experimental data. The study was undertaken by means of electron and optical microscopy on high purity Fe-C alloys with three different carbon contents, i.e. 0.13, 0.32 and 0.63wt%C. The particular technique employed in their treatment allowed them to discriminate between corner and edge nucleated particles. Further by appropriate correction, the measured number of nuclei in the plane of polish was converted to the surface density of particles in the unreacted austenite grain faces. In terms of modeling, Lange et al. [40], adopted classical nucleation theory and incorporated both the pillbox and the spherical cap models to evaluate the steady state nucleation rate of ferrite at the austenite grain boundaries. They found that only the pillbox nucleus shape with low interfacial energy can give satisfactory results compared to the experimental measurements for steady state nucleation. Figure 2-5 shows a vertical section of a disc-shaped pillbox nucleus.

\[
\gamma \begin{array}{c}
\sigma_{c}^c \\
\sigma_{c}^y
\end{array} \begin{array}{c}
\sigma_{c}^b \\
\sigma_{c}^{y}
\end{array} \gamma
\]

Figure 2-5 The vertical section of a coherent pillbox nucleus [40].

Following classical heterogeneous nucleation theory, Lange et al. [40] developed an expression for the steady state nucleation rate using the pillbox coherent model:

21
where, $\chi = \sigma_{\alpha\gamma}^e + \sigma_{\alpha\gamma}^{ob} - \sigma_{\gamma\gamma}$, $D_i$ is the appropriate diffusivity of the rate controlling species with an atomic fraction $X_i$ in the austenite matrix prior to transformation, $V_{\alpha}$ is the molar volume of ferrite, $\bar{a}_L$ is the average lattice parameter of ferrite and austenite, $\Delta G_V$ is the free energy change, $W$ is the strain energy associated with the nucleus (assumed to be zero), $\sigma_i$ indicate the interfacial energies as shown in Figure 2-5. The radius and the height of the critical nucleus, $r^*$ and $h^*$, are:

$$r^* = -\frac{2\sigma_{\alpha\gamma}^e}{\Delta G_V}$$  \hspace{1cm} (2-18)$$

$$h^* = -\frac{2\chi}{\Delta G_V}$$  \hspace{1cm} (2-19)$$

Applying the appropriate parameters to Equation (2-17) is a challenging task [41]. The unknown parameters that have to be quantified correctly are: $N$, $D_i$, $\chi$, $\sigma_{\alpha\gamma}^e$ and $\Delta G_V$.

Starting with the binary Fe-C system, the appropriate diffusivity of carbon in austenite [42,43] can be used and $\Delta G_V$ can be calculated assuming the critical nuclei has a composition of either equilibrium or the one that provides the maximum energy change [44,45]. Then on the assumption that the pillbox height is one lattice parameter [41], $\chi$ is obtained from Equation (2-19). Further, the value for $\sigma_{\alpha\gamma}^e$ should fall in the range of 20 to 40 mJ/m$^2$ in Fe-C alloys [41]. Then to reflect the experimental measurement of $\dot{I}_s$ with Equation (2-17), $N$ was estimated as $10^9$ sites/cm$^2$ for Fe-C alloys, which can also be used in ternary and quaternary systems [41]. This potential nucleation site density is substantially smaller than the number of available sites at austenite grain boundaries, i.e. $2 \times 10^{15}$ /cm$^2$. 

$$\dot{I}_s = \frac{2ND_iV_{\alpha}X_i^{1/2}}{\bar{a}_L^4(3kT)^{1/2}} \exp\left[\frac{-4\pi(\sigma_{\alpha\gamma}^e)^2\chi}{(\Delta G_V + W)^2 kT}\right]$$  \hspace{1cm} (2-17)$$
In ternary and quaternary systems, more complexity is involved in determining the above parameters. Three different alternatives can be considered for the nucleation process:

- paraequilibrium in which carbon volume diffusion in the austenite is rate controlling
- orthoequilibrium with mass transport controlled by volume diffusion of substitutional element $i$ in austenite
- orthoequilibrium limited by grain boundary diffusion of $i$.

Enomoto and Aaronson [46] found that orthoequilibrium with grain boundary diffusion of $i$ is the mechanism controlling ferrite nucleation in Fe-C-$i$ alloys. In a more delicate study, Tanaka et al. [41] analyzed the nucleation in Fe-C-Mn-$i$ alloys and suggested either paraequilibrium or orthoequilibrium limited by grain boundary diffusion of $i$ to obtain a nucleation rate consistent with experimental measurements. They also proposed that the possible synergism of $i$ and Mn in diminishing ferrite nucleation rates has to be considered.

So far, the coherent pillbox model with a radius of the critical nucleus size represents the most consistent way to analyze the nucleation kinetics of ferrite allotriomorphs at austenite grain faces in Fe-C, Fe-C-$i$ and Fe-C-Mn-$i$ [41]. However, it has been developed based on a number of controversial assumptions, which are difficult to verify. Moreover, Offerman et al. [36] reported that their measured nucleation rate could not be replicated by a pillbox model assuming interfacial parameters suggested in the literature [36] such that decreasing the activation energy by at least two orders of magnitudes is required to provide a decent agreement between experiment and prediction. Clearly, to resolve this controversy more detailed nucleation studies appear to be required and are now feasible with state-of-the-art characterization techniques.
2.1.2.2 Local equilibrium model for thickening of ferrite in Fe-C

Temporarily setting aside the effect of interface reaction, growth kinetics of ferrite allotriomorphs in Fe-C alloy is controlled by mass transport of carbon. Since the diffusivity of carbon in ferrite is comparatively high, the carbon concentration within growing ferrite is uniform, equal to \(c_{eq}^\alpha\) and excess carbon is rejected into austenite through the \(\alpha/\gamma\) interface. Thereby carbon redistribution in austenite is the rate-controlling process. During the early stage of thickening, particularly in coarse-grained specimens, the moving interfaces, which have an essentially disordered structure, can be described with reasonable accuracy as planar [47].

Considering a carbon mass balance in the system and assuming local equilibrium at the \(\alpha/\gamma\) interface, a linear carbon profile in semi-infinite austenite ahead of the interface and constant carbon diffusivity in austenite, Zener generalized the Dube analysis [48] and derived an analytical solution for parabolic growth of ferrite allotriomorphs given by the following equation:

\[
s = \frac{c_{eq}^\gamma - c_o}{\sqrt{(c_o - c_{eq}^\alpha)(c_{eq}^\gamma - c_{eq}^\alpha)}} \sqrt{D_c^\gamma t} \quad (2-20)
\]

where \(s\) is the thickness of the ferrite plate, \(c_o\) is initial carbon content of the alloy, and \(c_{eq}^\alpha\) and \(c_{eq}^\gamma\) are equilibrium carbon content of ferrite and austenite, respectively as depicted in Figure 2-6. Although Zener’s simplifications are not a solution of the underlying diffusion problem, analytical solutions for steady state diffusion problems confirm parabolic growth rates before soft impingement takes place.
To describe the overall growth kinetics including overlapping diffusion fields and concentration dependence of diffusivity, numerical solutions have been invoked [49,50,51]. The main underlying principles adopted by this kind of growth analysis can be summarized as follows:

- Early site saturation takes place even at low undercooling.
- Local equilibrium prevails at the interface. That is, the carbon concentrations at both sides of the $\alpha/\gamma$ interface are given by the equilibrium tie line. This implies that the net flux of carbon at the interface is zero, so that the incoming flux, $J_{in}$, due to carbon rejection from the growing ferrite is balanced by the outgoing flux, $J_{out}$, as result of carbon redistribution in the remaining austenite, i.e.:

\[
J_{in} = v(c_{eq}^\gamma - c_{eq}^\alpha) \quad (2-21)
\]

\[
J_{out} = -D_c \frac{\partial c}{\partial z}_{int} \quad (2-22)
\]

\[
\Delta J_{net} = J_{in} - J_{out} = 0 \quad (2-23)
\]

where $v$ is the interface velocity.
2.1 Literature Review

• To account for soft impingement due to overlapping diffusion fields within the austenite grain, the center of the austenite grain is a point of zero mass transfer:

\[ \frac{\partial c}{\partial z} = 0 \quad \text{at } z = \ell_o \]  \hspace{1cm} (2-24)

where \( 2\ell_o \) is the austenite grain size.

• Concentration dependency of carbon diffusivity is incorporated, for instance by using the carbon diffusivity proposed by Ågren [43] or by adopting the Trivedi-Pound [52] approach of a weighted average of the diffusion coefficient \( D \).

Another critical factor that has to be selected is the geometry of growth. Planar geometry can describe the diffusion situation only at the early stage of allotriomorph growth. At the later stage spherical geometry appears to be more appropriate where an outer shell of ferrite grows inward. Planar and spherical geometry are simple but do not reflect actual geometries. Thus, a model for the spherical growth of ferrite nucleated at the corner of Tetrakaidecahedron austenite grains, has been developed recently [53]. However, the unfilled space at the end of growth remains a controversial issue in this approach. Figure 2-7 shows the spherical and planar model geometry.

By applying the above assumptions the calculated ferrite layer thickness and its growth rate agree well with experimental values [50,51]. Therefore, diffusional controlled growth of ferrite in Fe-C alloy is reasonably well justified. Kamat et al. [51] compared planar and spherical geometry and suggested that spherical geometry is more suitable to describe the overall kinetics of ferrite growth.
2.1.2.3 Growth of ferrite in ternary and other multi-alloyed steels

In Fe-C alloys the carbon content of growing ferrite from parent austenite is clearly defined by the equilibrium phase diagram asserting that the long-range redistribution of carbon occurs during ferrite evolution, no matter how quickly the reaction proceeds depending on the applied cooling rate or undercooling. This is associated with the high diffusivity of carbon, as an interstitial species, in the iron lattice. In the presence of substitutional alloying ferrite can grow with or without equilibrium composition depending on the partitioning degree of these slow diffusing elements between the parent and product phases. At sufficiently high temperatures, i.e. close to $A_{e3}$, the redistribution of the substitutional atoms is thermodynamically required. The growth kinetics is then governed by long-range diffusion of these species in both participating phases and the equilibrium tie line constitutes the interfacial composition [54]. On the isothermal section of a ternary steel, Fe-C-$i$ as illustrated in Figure 2-8(a), this tie line is indicated by $\alpha_i$ and $\gamma_i$ for an alloy featuring nominal composition of $\gamma_o$. The growth rate is relatively slow and eventually ferrite evolves with
equilibrium content of all components, i.e. orthoequilibrium would be established at the end of transformation. Including in the left side of Figure 2-8(a) is also a typical composition profile of solute $i$ in ferrite and austenite. The orthoequilibrium formation of ferrite is hardly encountered in practice, however during nucleation due to very short diffusion distances, one can also presume it to be established.

![Figure 2-8 Schematic isothermal section of Fe-C-i system representing the interfacial concentration for ferrite growth under OE and NPLE conditions when the nominal composition of alloy is different.](image)

For the alloys inside the NPLE region, e.g. as indicated by $\gamma'_o$ in Figure 2-8(b), the supersaturation is high and the interface migrates faster than what substitutional controlled growth permits. In these circumstances ferrite tends to form with substitutional concentration close to the parent austenite, i.e. point $\alpha_1$ and local equilibrium might be held at the interface such that the interfacial composition is given by $\gamma_2$. This yields to the evolution of a substitutional spike in front of the migrating interface with a height of $\gamma_1 - \gamma'_o$. This spike is illustrated in the left side of the plot in Figure 2-8(b). The kinetics of ferrite formation behind this spike is then controlled by carbon diffusion away from the interface with carbon content as defined by the boundary of NPLE [32,34]. The term quasi-paraequilibrium was also
suggested to ferrite formation under this condition [35,54], although NPLE seems to be more accepted in the literature [34].

The spike of substitutional elements is likely to evolve with time and it is more realistic that ferrite first forms with paraequilibrium composition, i.e. this situation is characterized by partitioning of carbon and a frozen concentration profile of substitutional species. The growth under paraequilibrium condition occurs without any substitutional rearrangement even locally adjacent to the interface. However as the reaction further proceeds the growth rate tends to slow down, due to either exhausting the thermodynamic driving pressure and/or overlapping the carbon diffusion fields, then limited partitioning of substitutional elements close to the interface can be facilitated. This gives rise to the gradual evolution of a spike at the transformation front and constitutes a kinetic transition from paraequilibrium to NPLE condition [55,56].

Although it was addressed in early work [57], the potential transition between different growth modes has been an appealing subject for research worldwide recently. A review on deviation from local equilibrium and its rationale was provided by Hillert [54]. Oi et al. [58] investigated experimentally the boundary of kinetic transition from partitioning to no partitioning growth of ferrite in different Fe-C-Mn and Fe-C-Ni alloys. Although this transition is defined theoretically by the NPLE boundary, they observed that the exact boundary lies well above the NPLE yet inside the paraequilibrium region. The solute drag effect of substitutional elements, as quantified by Purdy and Brechet [59], was invoked to describe these findings such that in order to initiate the growth, the potential drag pressure has to be overcome by sufficient driving pressure i.e. sufficient undercooling below the PE boundary is required.
Odqvist et al. [55] have also analyzed the kinetic transition between PE and NPLE during isothermal ferrite formation theoretically in Fe-C-Ni alloys. Attempting to map the composition path taken by the interface during this transition, as shown in Figure 2-9, they employ an energy balance at the interface which facilitates finding simultaneously the interfacial concentration and the growth rate. Their quantification suggested that at the start of the reaction the interface features PE concentrations, i.e. point P. However, as growth proceeds the interfacial condition can no longer be at PE and a solute spike tends to form as the system approaches gradually the NP-LE condition, i.e. point F which shows the height of the solute spike. Apparently, depending on the initial composition of the alloy different composition paths would be predicted.

![Figure 2-9 The composition path of interfacial condition during isothermal growth [55].](image)

For a moving boundary, the interfacial energy balance asserts that the total energy dissipation has to be equal to the thermodynamic driving pressure available at the interface. The energy dissipation for moving boundaries arises from various irreversible processes. For example, energy is dissipated by diffusion to carry forward a segregation profile inside and a solute spike in front of a migrating interface. Further, in case of assuming a finite mobility for the
interface a contribution due to interface friction shall be introduced as well. Although it was predicted how the interfacial concentration deviates from local equilibrium as growth rate increase, Odqvist et al. did not elaborate what parameters would have to be adjusted in their model for description of experimental kinetics.

Recently Hutchinson and Brechet [56] proposed a transition between PE and NPLE to describe isothermal growth of ferrite in Fe-C-Ni systems where they had performed experimental studies. The ternary steels containing Ni were chosen by virtue of insignificant solute-interface interaction. Adopting a carbon diffusion model, it was revealed that in the early stage of growth the experimental kinetics agree well with the prediction using PE boundary condition while the subsequent ferrite formation can be described only by assuming NPLE interfacial concentration. This implies that for the alloy inside the NPLE region the growth would virtually stop, as the average carbon content of the untransformed austenite approaches the NPLE phase boundary. It was also observed that in alloys which lie above the NPLE limit the growth of ferrite occurs rather quickly at early stages and almost ceases at later stages. The maximum ferrite fraction was also detected to be different from PE prediction in this situation.

2.1.2.4 Retarding effect of solute atoms

In addition to accounting for the partitioning of solute atoms, the mutual interaction of the moving ferrite-austenite interface and alloying elements has to be considered in the kinetic model. Due to the presence of a high density of structural imperfections at grain and interphase boundaries, segregation of impurity atoms is likely at these interfaces, even in relatively high purity alloys. In case of moving boundaries, the segregation exerts a drag
force that yields to a drastic drop in the interface migration rate. This retarding effect of solutes on moving interfaces, which is referred to as *Solute drag effect*, was first discovered and analyzed in grain boundary migration during recrystallization and grain growth [60,61]. This idea was later extended to the migration of interphase boundaries [62] to explain the apparent discrepancies observed between measured and predicted kinetics. For instance, to resolve the disagreement between the measured and predicted kinetics of ferrite evolution, Militzer et al. [63] attempted to incorporate the solute drag effect into a diffusional model. They proposed a segregation model for Fe-C-Mn alloys where the solute drag of manganese at the $\alpha/\gamma$ interface changes the interfacial carbon activity. Although, their approach offered a decent description of the experimental results, it was a phenomenological treatment in which the velocity dependence of solute segregation was not addressed.

A detailed quantitative description of solute-interface interaction for moving grain boundaries was originally proposed by Lücke and Detert [60], and Cahn [61]. The term *drag force* stems from their treatment, in which the binding force on the segregated atoms inside the migrating interface region is integrated into an overall solute drag force. Assuming a symmetrical wedge shape well for the interaction potential inside the grain boundary and solving the flux equation for solute in this region, the segregation profile, $c_s(x)$, can be calculated. For moving boundaries, due to an asymmetry in the segregation profile the net drag pressure is not zero and it can be determined by accounting for the contribution of all segregated atoms over the entire interface region, i.e. from $-\delta$ to $+\delta$. According to Cahn’s treatment, the solute drag pressure, $P_{SD}$, which can be converted to the free energy dissipated per mole of substitutional atoms [64], is calculated by:
2.1 Literature Review

\[
\Delta G_{SD} = P_{SD} V_m = - \int_{-\delta}^{+\delta} \left[ c_S(x) - c_{S,0} \right] \frac{\partial E}{\partial x} \, dx
\]

(2-25)

where \( V_m \) and \( c_{S,0} \) are the molar volume and the bulk concentration of substitutional atoms, respectively, and \( \frac{\partial E}{\partial x} \) denotes the gradient of the interaction profile in grain boundary region. The term \( c_{S,0} \int dE \) was introduced into the above integral by Cahn and constitutes the main difference between his approach and that proposed by Lücke and Detert [60].

Introducing an asymmetrical interaction potential, Purdy and Brechet [59] extended Cahn’s solute drag theory to moving interphase boundaries. Alternatively, the kinetic effect of solute segregation to moving interfaces has been treated as Gibbs energy dissipation by Hillert [65] and was later extended to interphase boundaries for partitionless phase transformations by Hillert and Sundman [66]. All these treatments assume the interaction of a single species with the moving interface, however recently a number of attempts to model co-segregation have been reported in the literature as well [67,68].

Adopting the Purdy-Brechet approach to quantify the drag effect of Mo, Purdy et al. [69] attempted to model the formation of the distinctive bay in Fe-C-Mo alloys. Oi et al. [58] evaluated the maximum driving force required to overcome the solute drag force in Fe-C-\(i\) systems, thereby indirectly estimating a solute-boundary binding energy of \( \approx RT \) for Mn and \( \approx 0.5RT \) for Ni. Enomoto [64] refined the Purdy-Brechet theory by including the effect of carbon cosegregation with Mn on the ferrite-austenite interphase, i.e. considering a non ideal solution and introducing the Wagner’s description of the interaction between carbon and substitutional solutes. However, Enomoto’s approach to interpret the drag force in terms of energy dissipation was criticized by Hillert [70] who believes that his description of energy dissipation has to be discriminated from the drag force defined by Cahn. Only when the
thermodynamic properties inside the interface region are invariant with respect to composition and location [70], Cahn’s treatment provides similar results to those Hillert’s approach suggest.

It has to be noted that the treatment of Purdy-Brechet fails to predict a zero drag pressure for stationary interfaces. This artifact is not significant in the calculation provided in the original paper, since the assumed binding energy was taken to be much larger than $\Delta E$. Hillert and his coworkers [70] argued that neglecting the spike of substitutional elements in front of the moving interface yields the artifact in the Purdy-Brechet approach. At steady state the height of this spike is related to $\Delta E$, i.e. to the partition coefficient $k^{\gamma/\alpha} = \exp(-\Delta E/RT)$, and by assuming an ideal solution model for austenite, the energy consumed by pushing the spike ahead is given by [70]:

$$
\frac{G_{\text{Spike}}}{RT} = -X_{i,o} \ln k^{\gamma/\alpha} + (1 - X_{i,o}) \ln \frac{1}{1 - \frac{1}{X_{i,o}} - k^{\gamma/\alpha}} \quad (2-26)
$$

According to Hillert and Sundman [66] the drag force calculated using Cahn’s definition, i.e. Equation 2-25, includes as well the energy dissipation by the spike which is of finite value for $\Delta E \neq 0$. Therefore to predict a zero drag pressure for a stationary interface the contribution from the spike has to be accounted for [70], i.e.:

$$
\Delta G_{\text{SD Corrected}} = \Delta G_{\text{SD}} - G_{\text{Spike}} \quad (2-27)
$$

This correction might be sensible in the presence of a spike, i.e. when NPLE prevails or the interface deviates from PE and is in transition towards NPLE. However, as discussed before depending on reaction temperature and supersaturation, the ferrite-austenite interfaces can move relatively fast such that the interfacial condition is likely to remain at paraequilibrium. In these situations a solute spike does not existed in front of the interface and further, the
chemical potential difference of substitutional species is not zero, i.e. $\Delta E \neq 0$. Therefore, for
ferrite formation under paraequilibrium condition alternative means to correct the
aforementioned artifact are required. This problem will be revisited in section 2.2.2.4.

### 2.1.2.5 Mixed-mode model for ferrite growth

Austenite decomposition to ferrite involves the reconstruction of BCC from FCC crystal that
is accomplished by the individual jumping of substitutional atoms across the interface.
Simultaneously, carbon partitioning has to take place, presumably at a rate much higher than
this interface reaction. However, if the intrinsic interfacial friction becomes appreciable,
including the effect of interface reaction on growth kinetics is required.

According to the theory of thermally activated growth [71], the interface velocity, $v$ is
proportional to the driving force for interface migration, as given by:

$$v = M \Delta G$$  \hspace{1cm} (2-28)

where $\Delta G$ is the Gibbs free energy difference per mole across the interface and $M$ is the
interface mobility. In addition to OE, PE and NPLE assumptions in determining the driving
force for interface migration, this parameter can be calculated based on the local chemistry at
the interface or according to the average global concentration predicted by a “mean field”
approach.

In contrast to the local equilibrium approach of diffusion models, the interfacial carbon
concentrations are not constant. Carbon builds up at the interface as growth proceeds, it
changes from the initial concentration to approach the equilibrium carbon concentration of
austenite, e.g. from $c_o$ to $c_{eq}$, respectively. This change of interfacial carbon content is related
to non-zero carbon net flux at the interface and can be expressed by the following mass
transport equation:
Carbon volume diffusion and interface reaction are coupled together by the above equation to give the momentary interfacial carbon concentration, i.e. growth kinetics is mixed-mode controlled.

Van der Zwaag and his co-workers describe the kinetics of austenite decomposition in Fe-C, Fe-C-i and Fe-i systems successfully with the mixed-mode approach [72,73,53]. Although the model predictions seem promising, the interface mobility is treated as a fitting parameter which in some cases yields to unusual outcome, e.g. cooling rate dependency of the fitted mobility. Further, the interaction of manganese with the interface was neglected. Thus the proposed mobilities have to be considered as effective values.

2.1.2.6 Overall kinetics of ferrite formation

The overall kinetics of isothermal decomposition of austenite to ferrite, agrees well with the sigmoidal curve of the Avrami-equation [74] and its later modified version proposed by Umemoto [75]:

\[
f_a = 1 - \exp\left(\frac{-bt^n}{d^m_r}\right)
\]  

(2-30)

Here \( f_a \) is the normalized fraction of ferrite, \( b, n \) and \( m \) are empirically determined constants. In general \( b \) is a kinetic parameter that represents the combination of nucleation and growth rates and then depends on temperature. The \( n \) and \( m \) values in some cases are considered to be constant. The nominal values [76] for these two parameters expected for different nucleation situations, i.e. nucleation site saturation and nucleation and growth are outlined in Table 2-1.
2.1 Literature Review

### Table 2-1 Nominal values for n and m parameters [76]

<table>
<thead>
<tr>
<th></th>
<th>Site saturation</th>
<th>Nucleation and growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation sites</td>
<td>n</td>
<td>m</td>
</tr>
<tr>
<td>Grain surface</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Grain edge</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Grain corner</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

Campbell et al. [77], have found an average value of $n$ equal to 1.16 (0.88 < $n$ < 1.33) and Umemoto [78] reported values of $n$ in the range of 1.2-1.3. These values are less than that of pearlite, which fall in the range of 1.9-2.7 [77], and suggest ferrite nucleation takes place in the early stages of transformation such that nucleation site saturation occurs. The $m$ value reported by Umemoto [75], is between 1.2 and 1.3, which verifies nucleation occurs mainly on grain surfaces.

A model for the overall kinetics of ferrite formation during continuous cooling processes can be developed by adopting the rule of additivity [79] and applying the Avrami approach. A transformation is additive if the criterion of an isokinetics reaction is fulfilled. Mathematical interpretation of this criterion is that the rate of transformation has to be expressed by two separate functions of fraction transformed and temperature, such that:

$$
\dot{f} = \frac{df}{dt} = H(f)G(T) \tag{2-31}
$$

The differential form of Avrami’s equation, as given by the following expression, suggests that to satisfy the above condition $n$ has to be constant and only $b$ is a function of temperature:

$$
\frac{df}{dt} = b^{1/n} \left\{ n(1 - f) \left[ -\ln(1 - f) \right]^{n-1} \right\} \tag{2-32}
$$
Assuming an average value for \( n \) of about 0.9 and finding out the temperature dependency of \( b \), one can model the overall kinetics of ferrite formation during continuous cooling for low-carbon steels, readily [21].
2.2 Model Development

The purpose of this chapter is to delineate in depth the modeling methodology and strategy based on which the kinetic model for austenite to ferrite transformation has been developed. The prime goal of the present microstructural model is to describe the ferrite formation under industrial processing conditions, where the transformation kinetics is solely dictated by ferrite growth, i.e. the transformation starts from an austenite-ferrite microstructure or the applied cooling paths are such that nucleation site saturation occurs at the early stages of the reaction. Therefore, the current model deals with the growth kinetics of ferrite and to accomplish this, the mixed-mode approach was adopted as the main framework. Moreover, the kinetic effect of alloying elements, i.e. solute drag, was incorporated into the model in a rigorous way. Depending on the partitioning degree of substitutional elements, appropriate thermodynamic description of the system, i.e. PE or NPLE, can be selected for the simulations, however the transition between them is not considered here.

Integrating all the aforementioned features, the overall model consists of several modules, i.e. thermodynamic routine, carbon diffusion, mixed-mode module and solute drag part, which will be elaborated in the following sections.

2.2.1 Characterizations of the thermodynamics of ferrite formation

Thermodynamic information, which is an essential input into any kinetic model, is evaluated by means of Thermo-Calc version N. Thermo-Calc is a commercial/academic software developed by the Royal Institute of Technology in Stockholm. This integrated software utilizes the Fe2000 database to get the required data for low alloy steels. Table 2-2 indicates
the list of elements included in the Fe2000 database and the maximum permitted level for each element provided that the total alloying does not exceed 50 weight percent.

Table 2-2 List of elements included in Fe2000 database in their maximum permitted level (wt%).

<table>
<thead>
<tr>
<th>Al</th>
<th>B</th>
<th>C</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Mg</th>
<th>Mn</th>
<th>Mo</th>
<th>N</th>
<th>Nb</th>
<th>Ni</th>
<th>O</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ti</th>
<th>V</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>t</td>
<td>2</td>
<td>15</td>
<td>30</td>
<td>1</td>
<td>t</td>
<td>20</td>
<td>10</td>
<td>1</td>
<td>5</td>
<td>20</td>
<td>t</td>
<td>t</td>
<td>t</td>
<td>5</td>
<td>2</td>
<td>5</td>
<td>15</td>
</tr>
</tbody>
</table>

The kinetic model in this study has been developed under COMPAQ visual FORTRAN version 6.5. To link this application program to Thermo-Calc, the TQ-interface is incorporated.

Thermo-Calc version N is capable of evaluating the thermodynamic parameters only under complete equilibrium conditions, therefore for ferrite formation under orthoequilibrium assumption the phase boundaries, chemical potentials and driving pressure can be assessed readily. However, to quantify the thermodynamic information of a multicomponent system under paraequilibrium and negligible-partition local equilibrium assumptions appropriate subroutines have to be developed.

2.2.1.1 Paraequilibrium treatment

For the sake of transparency, the procedure steps to calculate the PE thermodynamic parameters of a ternary steel, i.e. Fe-C-i, are described here, although the approach can be extended simply to higher order alloying steels as well. Fortunately, the configuration of Gibbs energy of ferrite and austenite phases in PE condition can be presented as a pseudo binary diagram. Therefore, a section through the free energy surfaces of austenite and ferrite along the concentration ray of carbon is first made with the help of Thermo-Calc, which is schematically shown in Figure 2-10. Along the composition axis, which is characterized by
2.2 Model Development

carbon and an imaginary substitutional component, i.e. C and SC, carbon mole fraction changes while the ratio of the mole fraction of substitutional elements to iron remains constant (cf. Equation (2-9). For a given carbon mole fraction $X_C$, the pseudo-chemical potential of the substitutional component in phase $j$, can be expressed in terms of the chemical potentials of iron and alloying atoms, $\mu^j_F(X_C)$ and $\mu^i(X_C)$, respectively, as given by:

$$\mu^j_{SC}(X_C) = \frac{1}{1 + \sum_i \theta_i} \left[ \mu^j_F(X_C) + \sum_i \theta_i \mu^i(X_C) \right]$$

(2-33)

The paraequilibrium tie line, i.e. the carbon equilibrium composition of ferrite, $X^a_{PE}$, and austenite, $X^\gamma_{PE}$, is then determined by the common tangent line to the free energy curves, i.e.:

$$G^a + (X^\gamma_{PE} - X^a_{PE}) \left. \frac{\partial G^a}{\partial X_C} \right|_{X^a_{PE}} = G^\gamma$$

(2-34)

$$\left. \frac{\partial G^a}{\partial X_C} \right|_{X^a_{PE}} = \left. \frac{\partial G^\gamma}{\partial X_C} \right|_{X^\gamma_{PE}}$$

(2-35)

Figure 2-10 Section of the free energy surfaces of ferrite and austenite along the concentration ray of carbon for a given $X/X_F$ ratio.
In order to calculate the first derivative of $G^\alpha$ and $G^\gamma$ with respect to carbon mole fraction a continuous function is required, therefore a SPLINE curve was fitted to each Gibbs energy section of ferrite and austenite. The FORTRAN subroutine developed for assessment of PE phase boundary is included in Appendix II.

As an example the paraequilibrium phase boundaries were calculated at 700°C for the Fe-C-Mn system and the results together with those for orthoequilibrium, are illustrated as a ternary isothermal section in Figure 2-11. Apparently, the paraequilibrium boundaries fall inside the orthoequilibrium region, moreover its tie lines are almost parallel to the carbon concentration axis.

The essential thermodynamic parameter that the mixed-mode kinetic model employs is the driving pressure, based on which the velocity of the ferrite-austenite interface is evaluated. It should be kept in mind that equilibrium concentration cannot be attained at interfaces with finite mobility. Therefore, adopting the paraequilibrium treatment for the mixed-mode growth is referred to here as the case in which the interfacial driving pressure is determined with respect to paraequilibrium such that the system is forced to approach this constraint equilibrium when growth ceases. A similar concept could be applied if other thermodynamic description, e.g. NPLE, were assumed.

In the case of paraequilibrium treatment, during the mixed-mode ferrite formation, the interfacial composition in the parent phase, $X^\gamma_{\text{int}}$, changes from the initial carbon concentration of the alloy, $X_0$, to the paraequilibrium carbon content of austenite, $X^\gamma_{\text{PE}}$, as growth proceeds. The interfacial carbon concentration in ferrite, $X^\alpha_{\text{int}}$, is then chosen such that there is no difference in the chemical potential of carbon across the interface. Thus, $X^\alpha_{\text{int}}$ changes in accordance with the value of $X^\gamma_{\text{int}}$. Because of the higher diffusivities in ferrite the
carbon redistribution is assumed to be instant, i.e. the carbon concentration in ferrite is uniform and given by the interfacial value, $X_{\text{int}}^a$.

\[ \begin{align*}
0.08 & \quad 0.06 & \quad 0.04 & \quad 0.02 & \quad 0.00 \\
0.00 & \quad 0.01 & \quad 0.02 & \quad 0.03 & \quad 0.04 & \quad 0.05
\end{align*} \]

\[C \text{ mole fraction}\]

\[Mn \text{ mole fraction}\]

\[T=700^\circ C\]

\[\begin{align*}
(a) & \\
(b)
\end{align*}\]

Figure 2-11 Isothermal section at 700°C for Fe-C-Mn system, (a) shows paraequilibrium and orthoequilibrium phase boundaries as well as OE tie lines, (b) shows the iron rich corner.

The thermodynamic driving pressure, as depicted in Figure 2-12, is evaluated based on the local chemistry at the interface, i.e.:
2.2 Model Development

\[ \Delta G_{\text{int}} = (1 - X_{\text{int}}^a) \left[ \mu_{SC}^\gamma (X_{\text{int}}^\gamma) - \mu_{SC}^\alpha (X_{\text{int}}^\alpha) \right] \]  

(2-36)

Figure 2-12 Paraequilibrium pseudo-binary diagram illustrating the calculation of the chemical driving pressure at the start of ferrite growth where \( X_{\text{int}}^\gamma = X_o \).

2.2.1.2 Negligible partitioning local equilibrium boundaries

The thermodynamic procedure described in section 2.1.1.3 was adopted to calculate the NPLE boundary. A typical calculation of NPLE phase boundary at 700°C for Fe-C-Mn together with paraequilibrium and orthoequilibrium boundaries, are plotted in Figure 2-13. The FORTRAN code to perform the aforementioned procedure is given in Appendix III. The required data is retrieved from Thermo-Calc by calling appropriate subroutines defined in the TQ interface.
2.2 Model Development

Chapter 2

0.08

0.06

0.04

0.02

0.00

0.00

0.01

0.02

0.03

0.04

0.05

C mole fraction

Mn mole fraction

T=700°C

Orthoequilibrium

Paraequilibrium

NPLE

0.08

0.06

0.04

0.02

0.00

0.00

0.01

0.02

0.03

0.04

0.05

C mole fraction

Figure 2-13 Isothermal section of phase diagram at 700°C for the Fe-C-Mn system comparing NPLE, PE and orthoequilibrium boundaries.

2.2.2 Modeling the growth kinetics of ferrite

The two main approaches adopted in the present work to describe the growth kinetics of ferrite are the local equilibrium carbon diffusion model and the mixed-mode concept. The former is used solely for the sake of comparison and as will be discussed in the next chapter, its application seems to be restricted to steels containing more than 0.2wt%C, where the role of interface reaction can be neglected. In both approaches the carbon concentration profile inside the remaining austenite has to be quantified first therefore identical numerical procedures are implemented in this part of the kinetic model. However, it is the velocity of the ferrite-austenite interface that has to be calculated in a different way. In the carbon diffusion model, the balance of carbon flux locally at the interface aids to estimate the interface velocity while the mixed-mode methodology employs the intrinsic mobility and the driving pressure at the interface to characterize the growth rate of ferrite.
2.2 Model Development

Prior to solving the required differential equation pertinent to carbon diffusion in austenite, an appropriate geometry for the growing ferrite and the parent austenite phases has to be defined. Semi-infinite slab featuring planar geometry for the ferrite-austenite interface was adopted to analyze the thickening of ferrite allotriomorph, the morphology that tends to develop at the initial stage of transformation. The slab thickness is assumed to be the average austenite grain size. To describe the overall kinetics of ferrite evolution a spherical austenite grain is assumed such that ferrite constitutes its outer shell and grows toward the grain center. This configuration replicates adequately the growth of ferrite after nucleation site saturation at austenite grain boundaries, which was experimentally confirmed as shown in Figure 2-14. The physical methodology taken to develop diffusion and mixed-mode controlled models, as well as the numerical implementation of the outlined geometries, is described here.

2.2.2.1 Carbon diffusion controlled model

To calculate the carbon concentration profile inside the austenite, Fick's second law for moving boundary situation was employed. The change of carbon content in a specific location is related to two carbon fluxes, one is due to the movement of the axis frame and one arises from the concentration gradient, e.g. for planar geometry:

\[
\frac{dc}{dt} = \frac{\partial}{\partial z} (vc + D \frac{\partial c}{\partial z}) \tag{2-37}
\]

An implicit finite difference method (FDM) [80] was employed to solve this differential equation.
Figure 2-14 (a) Ferrite thin shell decorating austenite grain boundaries, ferrite formed partially at 735°C from austenite with grain size of 96μm in 0.17wt%C-0.74wt%Mn steel, followed by quenching to room temperature, (b) schematic representation of the ferrite growth as a spherical shell toward the center of austenite grain.
Ferrite formed at austenite grain boundaries grows with planar or spherical geometry toward the grain interior. In either case the austenite grain is discretize into several nodes as depicted in Figure 2-15a. The austenite grain with initial size of $2\ell_o$ is composed of $n$ nodes, while the ferrite layer of thickness $\ell$ has uniform carbon concentration identical to its interfacial value (e.g. in the diffusion model $c^\alpha = c^\alpha_{eq}$), such that it can be represent by one mesh.

As growth proceeds the only grid in ferrite becomes larger at the expense of the shrinkage in the parent austenite phase. To handle the problem of the moving ferrite-austenite interface, Murray-Landis [81] variable-grid method, which had been adopted by Tanzilli and Heckel for diffusional solid state transformations [82], was employed. Then considering different geometries, the concentration change of an internal node in austenite is given by:

$$\frac{dc_i}{dt} = \frac{\partial c_i}{\partial z_i} \frac{dz_i}{dt} + \frac{\kappa D_i}{z_i} \frac{\partial c_i}{\partial z_i} + \frac{\partial D_i}{\partial z_i} \frac{\partial c_i}{\partial z_i} + D_i \frac{\partial^2 c_i}{\partial z_i^2}$$  \hspace{1cm} (2-38)

where $c$ is the carbon concentration, $z$ is the distance from the origin, $D$ represent the carbon diffusivity in austenite, $\kappa$ is a geometry factor, i.e. 0 for planar and 2 for spherical geometry, and $i$ denotes the node number.
2.2 Model Development

The migration rate of an internal point in austenite is related to the interface velocity, \( v = \frac{d\ell}{dt} \), and its distance from the interface as for the assumed geometries are given by the following expressions:

**Planar:**
\[
\frac{dz_i}{dt} = \frac{l_o - z_i}{l_o - \ell} \frac{d\ell}{dt} \quad (2-39)
\]

**Spherical:**
\[
\frac{dz_i}{dt} = \frac{z_i}{l_o - \ell} \frac{d\ell}{dt} \quad (2-40)
\]

Local equilibrium is assumed at the ferrite-austenite interface such that interfacial carbon concentration remains constant at its equilibrium value given by the appropriate tie line selected, e.g. ortho-, para- or negligible partition local-equilibrium. To fulfill this condition the net flux of carbon at the interface has to be zero, so that the interface velocity can be evaluated based on the carbon mass balance at the ferrite-austenite interface:

\[
\Delta J_{int} = 0 \Rightarrow \frac{d\ell}{dt} = \frac{1}{(c_{eq}^l - c_{eq}^o)} D_e \left( \frac{\partial c}{\partial z} \right)_{int} \quad (2-41)
\]

For the configuration as depicted in Figure 2-15, the discrete form of these equations in austenite, as are provided for planar and spherical configuration in Appendix IV, can be evaluated by the following substitutions [80]: (for \( i=2, 3, ...n, \ i=1 \) corresponds to the interface at which concentration is given by the equilibrium value)

\[
\frac{dc_i}{dt} = \frac{c_{i+1}^j - c_i^j}{\Delta t} \quad (2-42)
\]

\[
\frac{\partial c_i}{\partial z_i} = \frac{c_{i+1}^j - c_{i-1}^j}{2\Delta z} \quad (2-43)
\]

\[
\frac{\partial^2 c_i}{\partial z_i^2} = \frac{c_{i+1}^j - 2c_i^j + c_{i-1}^j}{\Delta z^2} \quad (2-44)
\]

\[
\Delta z = \frac{l_o - \ell}{n - 1} \quad (2-45)
\]
where \( j \) denotes the time step. The selected time step has to satisfy the stability criterion, in terms of diffusivity and grid size, i.e.:

\[
\Delta t \leq \frac{0.5 \Delta z^2}{D_c^\gamma}
\]  

(2-460)

The boundary conditions, which have to be considered in the carbon diffusion model, are as follows:

- At austenite side of the interface, i.e. \( z = \ell_o - \ell \) for \( t > 0 \) \( c_{int}^\gamma = c_{eq}^\gamma \).
- Zero mass transfer at the center of austenite grain: at \( i=n \) for \( t > 0 \) \( c_{n+1}^j = c_{n-1}^j \).

According to the mass conservation principle no carbon leakage or addition is permitted in the system therefore at each time step the overall mass balance is performed to check the accuracy of the numerical solution, such that the fraction of austenite can be assessed using the following equation:

\[
c_0 = (1 - f_a) c_a^\alpha + f_a \bar{c}^\gamma
\]  

(2-47)

where \( c_0 \) and \( \bar{c}^\gamma \) denote initial and average carbon content of austenite. If this fraction would be different from the one calculated from the above finite difference procedure, then the interface location would have to be adjusted to satisfy the mass balance. This potential disagreement could perhaps be due to error accumulation in the numerical solution. In contrast to the planar case, more numerical steps are involved in determining the average carbon concentration of austenite for a spherical grain. The example of the mathematical steps and the associated numerical implications are described in Appendix V.

Figure 2-16 shows an example of the model predictions for ferrite growth in Fe-0.23wt%C alloy. Calculations were performed for planar geometry and an initial austenite grain size of...
50μm at the temperature of 745°C where the equilibrium interfacial concentrations $c_{eq}^a$ and $c_{eq}^r$ were calculated as 0.017 and 0.62wt%C, respectively.

![Figure 2-16 Carbon profile for various growth times calculated by diffusion model. Ferrite growth with planar geometry at 745°C from austenite of 50μm grain size in Fe-0.23wt%C was assumed.](image)

2.2.2 Mixed-mode model

In this approach, a similar FDM and node configuration as in the diffusional model was employed to evaluate the carbon concentration profile in untransformed austenite. However, in contrast to the diffusion-controlled model, the interface velocity is evaluated based on its intrinsic mobility and the chemical driving pressure, as expressed by Equation 2-28, i.e.:

$$v = \frac{dl}{dt} = M \Delta G_{int}$$  \hspace{1cm} (2-48)

where $M$ is the intrinsic mobility of the interface and $\Delta G_{int}$ denotes the thermodynamic driving pressure for the austenite to ferrite reaction which here is evaluated based on the local composition at the interface as depicted in Figure 2-12.
As a consequence of, and in contrast to the carbon diffusion model, the interfacial carbon concentrations at both sides of the interface are variable quantities under isothermal conditions, for instance the interfacial carbon of austenite changes from the initial to the equilibrium carbon concentration of austenite, i.e. from $c_0$ to $c_r$, as growth proceeds. This is a consequence of a non-zero carbon net flux, $J_{\text{net}}$, at the interface (cf. Equation 2-29). The change of the interface carbon concentration in time step $\Delta t$ during which the interface advances $\Delta \ell = v \Delta t$ is calculated using the carbon net flux at the interface. The interfacial carbon concentration of austenite is then assessed in each step using the discrete form of Equation 2-29, i.e. [83]:

$$c_{\text{int}}^\gamma (\ell^*, t^*) = c_{\text{int}}^\gamma (\ell^*, t) + [c_{\text{int}}^\gamma (\ell, t) - c_{\text{int}}^\alpha - D_c \frac{\Delta t}{\Delta \ell} \frac{c_{\text{int}}^\gamma (\ell^*, t^*) - c(2, t)}{\Delta z}] \quad (2-49)$$

where $\ell^* = \ell + \Delta \ell$, $t^* = t + \Delta t$ and $c(2, t)$ denotes the carbon content of the adjacent node to the interface.

To maintain the equality of the chemical potential of carbon across the interface the carbon composition of the growing ferrite, $c_{\text{int}}^\alpha$, has to be re-evaluated in each time step accordingly. Because of higher diffusivities in ferrite it is assumed that the carbon concentration in ferrite is uniform and is given by its interfacial content.

In order to prevent any numerical instability the criteria depicted in Equation 2-47 has to be fulfilled for $\Delta t$, hence the time step required to perform the evaluation of the new interfacial carbon concentration and new composition profile inside the remaining austenite, is readjusted continuously during growth. In the present numerical approach, this is accomplished by setting $\Delta \ell$ to a value, which is smaller than the node size, e.g. about $0.01 \Delta z$. 

52
Employing the mixed-mode approach and assuming two different mobilities, i.e. $M=0.38$ and 0.05 $\mu$m mol/Js, the carbon concentration profiles inside the remaining austenite for different growth times are shown in Figure 2-17.

Figure 2-17 Carbon profile for various growth times calculated by the mixed-mode model for reaction at 745°C in Fe-0.23wt%C alloy assuming planar geometry and (a) $M=0.05$ $\mu$m mol/Js and (b) $M=0.38$ $\mu$m mol/Js.
2.2 Model Development

The simulations assumed ferrite formation in Fe-0.23wt%C alloy at 745°C where the equilibrium carbon content of the interface at austenite side is 0.62wt%. The interfacial carbon concentration increases with time at a rate, which is related to the value assumed for the interface mobility. It has to be noted that at the extreme case, i.e. $M \rightarrow \infty$, the equilibrium carbon concentration is established at the interface right from the onset of ferrite growth so that the mixed-mode model prediction is consistent with that of the diffusion model.

2.2.2.3 Assessment of solute drag effect

The kinetic interaction of the alloying elements with the moving α/γ interface, i.e. solute drag effect, was incorporated into the mixed-mode model by introducing an effective driving pressure, such that the free energy dissipated by drag, $\Delta G_{SD}$ reduces the available chemical driving pressure at the α/γ interface, i.e.[84]:

$$\Delta G_{\text{eff}} = \Delta G_{\text{int}} - \Delta G_{SD}$$  \hspace{1cm} (2-50)

The migration rate of the interface is then calculated using the effective driving pressure. Here, to model solute drag the quantitative description of Purdy and Brechet [59] serves as starting point, therefore we shall elaborate it in detail. Treating the interface as a continuum media, they assumed an asymmetrical wedge shaped well for the interaction potential of the solute with the interface as delineated in Figure 2-18. Here, $2\delta$ is the interface thickness, $2\Delta E$ is the chemical potential difference for $i$ in austenite and ferrite, i.e. $\mu_i^\gamma - \mu_i^\alpha$, and $E_o$ is the binding energy of $i$ to the interface which is represented by the depth of the potential well.
2.2 Model Development

The segregation profile, $c_s(x)$, of the substitutional element inside the interface region is predicted by a flux equation, which consists of three terms reflecting the contributions due to the concentration gradient $\frac{\partial c_s}{\partial x}$, the potential gradient $\frac{\partial E}{\partial x}$ and the velocity of the migrating interface. For a boundary moving with quasi-steady velocity $v$, the net flux is zero and the concentration profile is given by:

$$\frac{\partial C}{\partial X} + \frac{C}{RT} \frac{\partial E}{\partial X} + V(C-1) = 0 \quad (2-51)$$

where $C$, $X$ and $V$ are dimensionless parameters defined by $C = c_s/c_{s\,o}$, $X = x/\delta$ and $V = v\delta/D_b$, respectively. Here, $c_{s\,o}$ is the bulk composition of solute atoms and $D_b$ is their diffusivity across the interface. For a given binding energy, the feature of the predicted segregation profile depends on the velocity and $\Delta E$, such that as the migration rate increases the profile tends to flatten out however the degree of its asymmetry becomes more pronounced. Further, the asymmetry also depends on $\Delta E$, for instance for a stationary interface only in the case of $\Delta E=0$ this intrinsic asymmetry is eliminated and the segregation profile would be similar to that for grain boundaries as considered by Cahn [61].

Solute atoms segregate at different sides of the moving interface where dissimilar gradients in the interaction potential exist, therefore they exert unequal and opposite forces on the
boundary. The resulting net drag pressure is not zero and can be calculated by Cahn’s formulation. The intensity of drag pressure for a given interface velocity depends primarily on the binding energy and $\Delta E$, the latter is a function of interfacial carbon concentration and is calculated from the assumed thermodynamic conditions. Therefore, $\Delta E$ has to be re-evaluated at each time step before being employed in the solute drag module.

Assuming a binding energy of $1.5RT$ and $\Delta E=0$, the variation of segregation profile with normalized velocity are presented in Figure 2-19(a). As velocity increases the resulting concentration profile flattens out while the degree of its asymmetry becomes more pronounced. To explore the influence of $\Delta E$, the segregation profiles formed inside a stationary interface ($V=0$) for various values of $\Delta E$ are plotted in Figure 2-19(b) as well. Note that for a non-moving boundary the degree of asymmetry in the concentration profile increases with the chemical potential difference, $\Delta E$, of substitutional constituents across the interface. Only in the case of $\Delta E = 0$ this intrinsic asymmetry is eliminated and the segregation profile is consistent with that for grain boundaries, as considered by Cahn [61].

According to Cahn’s theory any asymmetric profile is per definition associated with a solute drag pressure. Then by accounting for the contribution of all segregated atoms over the entire interface region, the energy dissipation by solute drag per mole of substitutional atoms is determined from Equation 2-25.
Figure 2-19 Segregation profile inside the interface region (a) for various normalized velocities and \( \Delta E=0 \) and (b) for different values of \( \Delta E \) for a stationary interface \( (V=0) \).
2.2 Model Development

2.2.2.4 Modification to Purdy-Brechet solute drag model

It is expected that the drag pressure vanishes gradually as the normalized velocity approaches to zero, this physical concept is valid for all values of assumed solute-interface binding energy or calculated $\Delta E$. However, adopting the Purdy-Brechet approach to evaluate the drag pressure leads to an apparent artifact for stationary interfaces when $\Delta E \neq 0$ is considered. The problem arises from the presence of asymmetry in the interaction potential wedge and the resulting asymmetric segregation profile for zero interface velocity as evident in Figure 2-19(b).

For example, if the paraequilibrium description is employed in mixed-mode growth, the chemical potential difference of the substitutional solute, e.g. Mn, does not approach zero when the growth ceases at the end of the reaction. Accordingly, a non-zero drag pressure would be predicted if the Purdy-Brechet quantification were adopted preventing the system from reaching equilibrium. Therefore, it is imperative to remove this artifact by accounting for the intrinsic asymmetry in the interaction potential well. In the present work, it is proposed that the solute drag pressure is evaluated with new concentration and potential terms, which correct for the intrinsic asymmetry as a function of $\Delta E$, i.e.:

$$C_{\text{New}} = C \exp\left(\frac{\Delta E}{RT} X\right)$$  \hfill (2-52)

$$\frac{\partial E}{\partial X}_{\text{New}} = \frac{\partial E}{\partial X} - \Delta E$$  \hfill (2-53)

Then the drag pressure, or in other words the energy dissipated by solute drag, is calculated based on these newly introduced parameters as:

$$\Delta G_{SD} = -c_{S,0} \int_{-1}^{1} (C_{\text{New}} - 1) \frac{\partial E}{\partial X}_{\text{New}} dX$$  \hfill (2-54)
Using the above adjustment the drag pressure vanishes completely when the interface is brought to halt for all values of $\Delta E$. Figure 2-20 compares the predictions of the modified and the original version of the Purdy-Brechet solute drag model, where the binding energy of $1.5RT,-4kJ/mol$ for $\Delta E$ and $X_{s,e}=0.01$ are assumed for the calculations. Apart from the drop of drag pressure to zero for stationary interface, the modified version predicts less drag pressure for all velocities compared to the original approach and the peak of solute drag is slightly shifted from $V \approx 1.8$ to $V \approx 2$.

![Figure 2-20](image)

*Figure 2-20 Comparison of the energy dissipated by solute drag for $E_s=1.5RT$ and $\Delta E=-4kJ/mol$, adopting the Purdy-Brechet model and the modified solute drag approach.*

It is imperative to emphasize that in the present analyses the modified solute drag approach is employed to evaluate all drag forces. The reason for this adjustment is the fact that the isothermal kinetics cannot be captured accurately at the final stages of reaction. However, as reported previously [84], the original Purdy-Brechet description of the solute drag effect can still be applied successfully to continuous cooling cases, in which the thermodynamic driving
pressure for growth increases with undercooling while simultaneously the drag pressure
tends to decrease. Then the artifacts of the Purdy-Brechet approach do not affect its general
predictive ability for continuous cooling cases. However, the interpretation of the resulting
quantities for $D_b$ and $E_o$ may be of even more limited value.

2.2.3 Crucial parameters in the kinetic model

The integrated growth model as outlined above employs parameters which are defined
clearly in terms of their physics. Diffusion controlled reaction, and in part mixed-mode
growth rely on the quantification of carbon concentration in austenite, therefore the
diffusivity of carbon, $D_c^r$, is of common significance in both modeling approaches.
Fortunately the diffusion coefficient of carbon in austenite has been characterized accurately
by many researchers [42,43,85], and since no discernible influence of Mn, Si and Mo on
carbon diffusivity was reported, here the expression proposed by Agren, which is a function
of temperature and carbon concentration, is adopted for all calculations [43]:

$$D_c^r (m^2 s^{-1}) = 4.53 \times 10^{-7} \left[ 1 + Y_c (1 - Y_c) \frac{8339.9}{T} \right] e^{\left(-\frac{3.22}{T} \times 10^{-7} \tau_{17767-26436 Y_c}\right)} \tag{2-55}$$

where $Y_c = X_C/(1-X_C)$, represents carbon site fraction in the interstitial sublattice.

Apparently the most crucial kinetic parameter that the mixed-mode growth depends on is the
intrinsic mobility of the ferrite-austenite interface, i.e. $M$. This physical quantity is related to
the jump frequency of substitutional species, including iron atoms, across the interface that
leads to local reconstruction of BCC crystal from FCC lattice. Conceptually it is expected
that both local composition and structure of the interface affect the mobility, however no
conclusive theoretical description of these dependencies has been provided yet. Among a few
attempts to define the mobility in terms of the physical features of the interface, Turnbull's model [86] for grain boundaries is presented here for instance, although it overpredicts the experimental data of grain growth in pure iron [87] and moreover it relies on parameters that are difficult to determine accurately, i.e.:

$$M = \frac{\delta D_{GB} V_m}{b^2 RT}$$

(2-56)

where $\delta$ is the interface thickness, $b$ is the interatomic distance and $D_{GB}$ is the grain boundary diffusivity. Further, due to the fine scale and discontinues nature of the reaction interface, there is, at least currently, no experimental means by which the mobility can be characterized quantitatively. Treating the interface migration as a thermally activated process, one can consider a simplified version of the above equation in the form of an Arrhenius temperature dependence as given by:

$$M = M_o \exp\left(\frac{-Q}{RT}\right)$$

(2-57)

where $M_o$ is the pre-exponential factor and $Q$ represents the activation energy of the rate controlling process. As an attempt to determine these two parameters, Hillert [87] analyzed the kinetic data pertinent to grain growth in zone-refined iron and suggested the following mobility:

$$M(cm\ mol/Js) = 5 \times 10^5 \ exp\left(\frac{-144kJ/mol}{RT}\right)$$

(2-58)

This mobility also had been applied to massive austenite to ferrite transformation in low carbon steels showing satisfactory agreement with the experimental data. A more recent quantification of ferrite-austenite mobility for binary Fe-Mn alloys has been carried out by Krielaart and van der Zwaag [83]. They described the measured kinetics of ferrite formation, for different Mn contents and cooling rates, solely by means of an interface-controlled
growth model treating the mobility as an adjustable parameter. The overall mobility was proposed as:

\[
M (cm\,mol/Js) = 5.8 \exp\left(\frac{-140kJ/mol}{RT}\right)
\]  \hspace{1cm} (2-59)

in which the activation energy is almost identical with the one suggested by Hillert. However, the pre-exponential value reported by Hillert is about five orders of magnitude larger than that of Krielaart and van der Zwaag. Clearly, there is a great deal of uncertainty about the actual value of the intrinsic mobility. Assuming Hillert’s mobility in the mixed-mode model would lead to an interface reaction that occurs so quickly to not play any kinetic role such that the model would predict a transformation entirely controlled by carbon diffusion.

Consequently, in the present simulations the following assumptions are made regarding the intrinsic mobility. The activation energy of 140kJ/mol is taken and \(M_0\) is essentially an adjustable parameter. As the starting point to perform the simulations, the value proposed by Krielaart and van der Zwaag [83] is adopted for \(M_0\) and re-adjusted when required to describe the experimental kinetics.

Incorporation of the solute drag module into the mixed-mode model is associated with introducing additional parameters. In terms of drag pressure two main physical characteristics have to be defined, i.e. the interaction energy between the interface and the segregated solute, \(E_o\), and the diffusivity of this solute across the interface region, \(D_o\). Unfortunately, neither of these quantities can be measured directly by means of available experimental techniques, however the physically expected range of them can be derived as an order of magnitude estimate. For instance, Auger electron microscopy on the fracture surface of austenite grains in Fe-C-i systems [88], revealed that among Mo, Mn and Ni, the
2.2 Model Development

enrichment factor is the highest for Mo, and decreases in the order of Mn and Ni. Moreover, adopting the co-segregation model of Guttmann [89], the binding energy of solute to grain boundaries was estimated as 18, 9 and 5kJ/mol for the above elements, respectively. Oi and his coworkers [58] adopted the methodology proposed by Purdy et al. [69], i.e. balancing the driving pressure with solute drag force, and determined the following binding energies to ferrite-austenite interfaces: \( RT \) for Mn and \( 0.5RT \) for Ni. These values are consistent with the findings of Enomoto [64,88].

A binding energy in the order of \( RT \) for Mn and Ni is assumed here, however as will be addressed in the following chapter, the analyses of ferrite formation suggest that for adequate description of the experimental kinetics a temperature dependency for \( E_o \) is required, i.e.:

\[
E_o = A_e + B_e T
\]  
\[(2-60)\]

where the slope and intercept are treated as adjustable parameters. Thus, \( E_o \) is employed as an effective binding energy.

Definitely, the diffusivity of segregating solute across the interface is the parameter with the least certainty regarding its estimation. The nature of this atomic jump process seems to be quite different from that along grain boundaries, although it is expected to be a few orders of magnitude larger than the bulk diffusivity in austenite. For instance \( D_b \) was assumed to be larger by a factor of 1000 than the bulk diffusivity in some simulations [64,90] while a value close to the average of ferrite and austenite bulk diffusivity was taken for \( D_b \) as well [56]. In the present simulations an Arrhenius temperature variation is adopted for the normalizing factor of the interface velocity, i.e. \( D_b/\delta \), as given by:

\[
\frac{D_b}{\delta} = \frac{D_o}{\delta} \exp\left(-\frac{Q_b}{RT}\right)
\]  
\[(2-61)\]
where similar to the case of solute migration along the grain boundaries, the activation energy, $Q_b$, is considered to be half of the one for bulk diffusion in austenite. For example this quantity for Mn and Ni is set as 132 and 137kJ/mol, respectively [91]. The diffusivity in austenite is used as a reference point even though it is smaller than the diffusivity in ferrite. However, below the Curie temperature (770 °C) ferromagnetic ordering decreases diffusion coefficients and the data available for diffusion in paramagnetic ferrite cannot be extrapolated to the temperature range of transformation. The pre-exponential factor, $D_0/\delta$, constitutes then another fitting parameter.
2.3 Model Application

2.3.1 Analysis of allotriomorph thickening in Fe-C alloys

In this section the thickening of ferrite allotriomorphs is analyzed for binary Fe-C systems. This analysis deals with a growth geometry where ferrite forms along austenite grain boundaries and features parabolic growth, both in lengthening and thickening, at the early stage of the reaction, i.e. prior to the impingement of carbon diffusion fields. Therefore, as also confirmed experimentally [92,93], the thickness, \( s \), varies with the reaction time, \( t \), as:

\[
s = \alpha \sqrt{t}
\]  

(2-62)

where \( \alpha \) is the parabolic rate constant.

The experimental measurement of allotriomorph growth is a challenging task and comparatively few results have been reported. There is noticeable data scattering, such that substantial variations in thickness from one to another allotriomorph in a given specimen has been observed [93]. This has been in part attributed to the presence of facets on the ferrite-austenite interface of ferrite allotriomorphs, which otherwise is expected to be disordered. Further, in many cases the thickness is measured in the plane that may not pass through the center of the allotriomorph, i.e. it is not normal to the grain boundary, which gives rise to the so-called stereological error. Most of the published data suffer from inaccuracy originating from these measuring complications. However, to improve the precision of the measured growth kinetics, the experimental technique developed by Bradley et al. seems to provide more reliable data. A summary of their measurements [92] of parabolic rate constants in three different Fe-C alloys containing 0.11wt%, 0.23wt% and 0.42wt%C is replicated in Figure 2-21. The examined temperatures range from 740 to 815°C. As expected, for each individual alloy, as reaction temperature decreases the rate of growth increases. Further, the
specimen with the highest carbon level, i.e. 0.42wt%, represents the smallest parabolic rate constant for all the investigated temperatures.

\[ \text{CO}_E = L \cdot J \cdot \text{CO} \cdot \text{M} \cdot \text{CO} \]

![Graph](image)

*Figure 2-21 Experimental parabolic rate constant in Fe-C alloys [92]*

### 2.3.1.1 Prediction of carbon diffusion model

The growth of ferrite allotriomorphs has traditionally been assumed to be controlled by carbon diffusion in austenite. However, considerable discrepancies between the measured parabolic rate constant and the predictions from diffusion models can be frequently found for several binary Fe-C systems in the literatures [93]. To examine the predictive capability of the carbon diffusion model, an attempt has been made to replicate the experimental data presented in Figure 2-21. The natural starting point is to utilize the analytical solution for the thickening of allotriomorphs as proposed by Zener [48]:

\[
\frac{2(c_{eq}^{r} - c_{eq}^{a})}{c_{eq}^{r} - c_{eq}^{a}} \sqrt{D_c^{r} / \pi} = \alpha, \exp(\alpha^2 / 4D_c^{r}) \left[ 1 - \text{erf} \left( \frac{\alpha}{2\sqrt{D_c^{r}}} \right) \right] \tag{2-63}
\]
2.3 Model Application

where \( c_{eq}^r \) and \( c_{eq}^a \) denote the equilibrium carbon content of the interface in austenite and ferrite sides, respectively, \( c_0 \) is the nominal carbon level in the alloy and \( D_C^r \) is the carbon diffusivity in austenite. The analytical solution is applicable only for the growth period before soft impingement. Moreover, in this approach a concentration independent carbon diffusivity in austenite is assumed. However, in the final solution as expressed by Equation 2-63, \( D_C^r \) can be evaluated based on various carbon concentrations, e.g. using an average carbon concentration in front of the ferrite-austenite interface, e.g. \( (c_0 + c_{eq}^r)/2 \), taking the interfacial carbon content of austenite, \( c_{eq}^r \), or considering initial carbon content of alloy, \( c_0 \).

Then, the calculated parabolic rate constant is quite sensitive to the value taken for the carbon diffusivity as illustrated in Figure 2-22 for Fe-0.11wt%C, where the experimental data are also included for the purpose of comparison. To evaluate the carbon diffusivity in austenite, the expression proposed by Ågren [43] was adopted in all the calculations.

![Figure 2-22 Zener predictions for parabolic rate constant and the measured [92] data in Fe-0.11wt%C](image-url)
Independently from the selection of the diffusion coefficient, it is evident that the analytical solution significantly overpredicts the measured growth rate in Fe-0.11wt%C for all examined temperatures. Although, adjusting the diffusivity led to smaller discrepancy with respect to the experimental data at the lowest reaction temperature, i.e. 745°C, no noticeable improvement was attained for the temperature of 815°C. This can be described by the larger difference between the value of \( \frac{(c_0 + c_{eq})}{2} \) and \( c_{eq}^{\nu} \) (or \( c_0 \)) as the growth temperature decreases.

One of the main drawbacks of the above analysis is that a variable diffusivity which is physically more sensible, cannot be employed in the analytical solution. Further, it is obvious that none of the above values for carbon concentration, i.e. average carbon concentration, the initial carbon content of the alloy or interfacial carbon content, can represent the exact carbon composition profile ahead of the interface. Therefore, it is required to utilize a more realistic treatment, i.e. a numerical solution, to overcome these simplified assumptions. The advantage of employing it to predict the growth kinetics of ferrite allotriomorph is its capability to account for the variable carbon diffusivity, e.g. Equation 2-55. This numerical approach was subsequently used to estimate the parabolic rate constant of the three Fe-C alloys. Both the model predictions and the experimental values are represented in Figure 2-23. For the purpose of comparison the predictions of Zener's analytical solution assuming average carbon concentration, i.e. \( \frac{(c_0 + c_{eq})}{2} \) to assess \( D_{C}^{\nu} \) are also included. The first glance at the prediction for all the examined alloys revealed that there is a good agreement between the analytical solution (Zener's equation) and the numerical solution. Further, for the alloys containing 0.11 and 0.23wt%C, the predictions of the numerical diffusion model are considerably above the measured data outside the
experimental error for all investigated temperatures. The degree of this disagreement tends to diminish as the carbon level of the investigated alloy increases, such that eventually the diffusion model can replicate the reported values of the rate constant in the Fe-0.42wt%C system.

2.3.1.2 Prediction of mixed-mode model

The failure of the carbon diffusion model to predict adequately the experimental growth kinetics of low-carbon alloys, i.e. with carbon contents of 0.23wt% and lower, indicates that another type of atomic phenomenon has to be operative. For the Fe-C alloys it can be ruled out that inappropriate evaluation of either $D^c_C$ or the interfacial composition causes this issue, since in Fe-C alloys the quantitative description of carbon diffusivity in austenite and ferrite-austenite boundaries in the Fe-C phase diagram are well established. Therefore, it is imperative in these circumstances to account for the kinetic role of the interface reaction rigorously. In particular the contribution of interface reaction tends to be more significant with decreasing the carbon content of alloy, such that as carbon concentration approaches to zero the growth kinetics of ferrite would solely be an interfaced-controlled one. These two atomic events, i.e. the reaction at the interface and the redistribution of carbon atoms in the remaining austenite, are coupled together elegantly in the framework of the mixed-mode model as explained in section 2.1.

The key parameter in the mixed-mode model is the intrinsic mobility of the ferrite-austenite interface, with a temperature dependence that can be described by an Arrhenius relationship, i.e. Equation 2-57. As outlined earlier, this mobility is used as an adjustable parameter.
2.3 Model Application

Figure 2-23 Comparison of the measured [92] parabolic rate constant with the prediction of the carbon diffusion model for (a) Fe-0.11wt%C, (b) Fe-0.22wt%C and (c) Fe-0.43wt%C alloys.
2.3 Model Application

The parabolic growth is described with a constant, \( \alpha \), which can be partially expressed in terms of interfacial carbon concentrations that remain constant during the isothermal ferrite formation, provided that local equilibrium at the interface prevails. In the carbon diffusion model, the ferrite-austenite interface is in equilibrium with respect to carbon therefore the condition for the parabolic thickening of allotriomorphs is certainly met. In contrast, in the mixed-mode model due to a non-zero net flux of carbon across the ferrite-austenite interface the interfacial carbon contents vary as growth proceeds. Thus, by definition \( \alpha \) is no longer constant and per se some deviations from the parabolic regime are expected.

This inherent effect is more pronounced at early stages of ferrite growth, when a relatively quick carbon built up occurs at the interface. As soon as the interfacial carbon level approaches its equilibrium value, i.e. \( c_{eq}^i \), the growth becomes carbon diffusion-controlled. Thus, the mixed-mode approach provides a smooth transition from an interface- to a diffusion-controlled mode. The period, during which growth is mainly governed by interface reaction, is characterized by a marked deviation from the parabolic growth behavior. This period tends to be shorter when a larger value for the interface mobility is assumed. To elaborate the discussion and as an example, the predictions of the mixed-mode approach are illustrated in Figure 2-24 for allotriomorph thickening in Fe-0.23wt%C at 775°C for two different mobilities \( M_0=5.8 \) and 1.27 cm mol/Js. Included in this figure is the prediction of the carbon diffusion model as well as the experimental data points [92]. It is seen that neither the diffusion model nor the mixed-mode approach, assuming \( M_0=5.8 \) cm mol/Js, can capture the measured thickness. The calculation using \( M_0=1.27 \) cm mol/Js seems to provide an adequate description of the experimental kinetics, although it does not follow the parabolic
growth. Besides, it is evident that the deviation from linearity is more significant for this mobility, i.e. $M_0 = 1.27$ cm mol/Js, compared to that for $M_0 = 5.8$ cm mol/Js.

![Figure 2-24 Measured allotriomorphs thickness and the predictions of mixed-mode model assuming $M_0 = 5.8$ and 1.27 cm mol/Js, as well as the calculation of the carbon diffusion model ($M_0 = \infty$) for growth at 775°C in Fe-0.23wt%C.]

The above argument implies that in terms of allotriomorph thickening, the prediction of the mixed-mode model consists of two growth modes: a initial non-parabolic part which is governed primarily by the interface reaction and the later stage where carbon diffusion is the main controlling step. The experimental growth kinetics reported in the literature for a given composition is usually expressed in terms of a parabolic rate constant. Unfortunately, the exact data points similar to the ones depicted in Figure 2-24, are seldom reported in the literature. Thus two alternative approaches exist to analyze the experimental kinetics of parabolic growth in the framework of the mixed-mode model and to find the appropriate value for the mobility. The slope of the second stage, i.e. the parabolic portion of the model prediction, can be compared with the reported $\alpha$, or alternatively, the exact measured data
points, if they are available, are used for the comparison with the calculated growth kinetics. Figure 2-24 shows that the model with $M_0=1.27 \text{ cm mol/Js}$ can capture the experimental data reasonably and the slope of its linear part, does agree well with the linear fit to the measured data points. As is outlined in the following paragraphs, it was found that overall, the mixed-mode model assuming $M_0=0.78 \text{ cm mol/Js}$ is capable of predicting the thickening kinetics of ferrite at various temperatures in three Fe-C alloys featuring carbon content ranges between 0.11 to 0.4wt%. For the present case, i.e. allotriomorph thickening at 775°C in Fe-0.23wt%C, using this mobility predicts an overall slope of $0.8 \mu\text{m s}^{-1/2}$ in the $s$ versus $\sqrt{t}$ plot, which concurs with the experimental slope and lies within the scattering band of the reported $\alpha$, i.e. $0.6\pm0.2 \mu\text{m s}^{-1/2}$. Therefore, either of the 1.27 or 0.78 (cm mol/Js) quantities can be selected for $M_0$ in Fe-0.23wt%C. The implication is that the intrinsic mobility of ferrite-austenite interface can be determined reasonably well from the analysis of allotriomorphs thickening by mixed-mode model. The error of the proposed mobility is likely to be less than one order of magnitude.

Since the reported parabolic rate constants are the only data available for all three Fe-C alloys they are considered in the analysis of allotriomorph thickening and compared with the parabolic part of the mixed-mode model predictions. Since the total time during which the experimental measurements had been carried out is not available, the simulation time is assigned to be the time for the onset of soft impingement in an austenite grain of 200μm size. This grain size is consistent with that used for allotriomorph thickness measurement [92], i.e. ASTM 1-2\textsuperscript{1}. Attempts then have been made to replicate the experimental $\alpha$ of Fe-C alloys presented in Figure 2-21 by changing the value of the mobility term. The slope predicted by

\textsuperscript{1} N(number of grains per unit of area, inch square, in 100X magnification)=$2^{n-1}$
the mixed-mode model was determined from the stage in which the growth is parabolic. The results including the prediction using the Krielaart and van der Zwaag mobility, i.e. $M_0=5.8$ cm mol/Js, and the experimental values of parabolic rate constant for ferrite formation in three Fe-C alloys are illustrated in Figure 2-25. For the comparison purpose the calculations of the diffusion model are also included.

It is quite obvious that the calculations using $M_0$ of 5.8 (cm mol/Js) overpredict the measured kinetics of the 0.11 and 0.23wt%C alloys, with the discrepancy being larger for the lower carbon content. However, for the Fe-0.42wt%C alloy, this assumed mobility provides rather good agreement with the experiment. As anticipated from the concept of mixed-mode modeling approach, the role that reconstruction of BCC from FCC plays in overall kinetics tends to be more profound when the carbon content of parent austenite decreases, such that eventually the overall kinetics becomes solely interface-controlled in pure iron.

Attempting to find a unique mobility that would be able to replicate the experimental $\alpha_t$ for all the investigated Fe-C alloys, gives a value of 0.75 cm mol/Js for $M_0$. As shown in Figure 2-25, the model predictions using this mobility show good agreement for all carbon levels and the investigated temperature range.

This corresponds to a mobility which is 0.13 times smaller than the value obtained from the studies in the Fe-Mn systems by Krielaart and van der Zwaag. Therefore, it is concluded that although accounting for the interface mobility is quite essential, no universal intrinsic mobility can be proposed for all chemistries. This constitute a main challenge of using the mixed-mode model, i.e. the model relies on the unknown parameters that first here to be determined for each alloying system by means of fitting practices.
Figure 2-25 Experimental data [92] of parabolic rate constant and prediction of mixed-mode model assuming mobility of 5.8 and 0.75 cm mol/Js for (a) Fe-0.11wt%C, (b) Fe-0.23wt%C and (c) Fe-0.42wt%C alloys. The predictions of the diffusion model are included as well.
2.3 Model Application

2.3.2 Analysis of allotriomorph thickening in Fe-C-i systems

2.3.2.1 Comments on the experimental data

The major aim of this section is to analyze the growth of ferrite allotriomorphs in ternary Fe-C-i systems that contain either Mn or Ni as the only substitutional element. Primarily, the predictive capability of the mixed-mode model to replicate the measured kinetics is going to be examined. Subsequently, the incorporation of the solute drag effect into the mixed-mode model and the physical relevance of the resulting interface parameters will be discussed.

The experimental thickening rates, against which the model is examined, were taken from published data for Fe-0.12wt%C-3.1wt%Mn, Fe-0.12wt%C-3.3wt%Ni [62] and Fe-0.21wt%C-1.52wt%Mn [34]. The ranges of investigated temperatures to quantify the allotriomorph thickness are presented in Table 2-3. Included in the table are also the theoretical Ae3 temperatures calculated based on the different thermodynamic assumptions, i.e. orthoequilibrium, paraequilibrium and negligible partitioning local equilibrium, by means of Thermo-Calc software.

<table>
<thead>
<tr>
<th>Alloy composition, wt%</th>
<th>OE $T_{Ae3}$, °C</th>
<th>PE $T_{Ae3}$, °C</th>
<th>NPLE $T_{Ae3}$, °C</th>
<th>$T_{meas}$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-0.21C-1.52Mn</td>
<td>792</td>
<td>772</td>
<td>733</td>
<td>725-735</td>
</tr>
<tr>
<td>Fe-0.12C-3.1Mn</td>
<td>771</td>
<td>732</td>
<td>588</td>
<td>550-650</td>
</tr>
<tr>
<td>Fe-0.12C-3.3Ni</td>
<td>772</td>
<td>742</td>
<td>670</td>
<td>650-720</td>
</tr>
</tbody>
</table>

Bradley and Aaronson [92,62] measured the ferrite thickness at austenite grain boundaries using room temperature, optical microscopy of the specimens, which had been reacted...
isothermally at the transformation temperature for different times followed by quenching. To minimize structural and stereological errors of the measurements, a particular austenitization technique was employed. This method tends to align the grain boundaries perpendicular to the intended plane of polish. The obtained parabolic growth constant for 0.12wt%C-3.1wt%Mn and 0.12wt%C-3.3wt%Ni steels are summarized in Figure 2-26. Moreover, to appreciate the quality of the measured kinetics in terms of parabolic growth, typical measurements of thickness variation with the square root of time for the Ni steel are duplicated in Figure 2-27. Despite minor scattering, ferrite thickens linearly with $\sqrt{t}$ and the growth looks to be reasonably parabolic for this system.

Figure 2-26 Experimental Measurements of parabolic growth rate constant of ferrite in C-Mn and C-Ni steels [34, 62].
2.3 Model Application

Figure 2-27 The measured thickness of ferrite allotriomorph at different growth temperatures in Fe-0.12wt%C-3.3wt%Ni alloy [94], the solid line represents linear regression.

Alternatively, Purdy and coworkers [34] carried out the annealing of diffusion couples to obtain the growth kinetics of ferrite in Fe-C-Mn alloys. The diffusion couple was constituted of a pure iron layer deposited electrolytically onto a polished martensitic segment of C-Mn steel with the desired composition. The couple was upquenched to the single austenite field, where martensite reversion to austenite occurred rather promptly, then quenched down to the target growth temperature in the two-phase region. The growth of the ferrite layer into
austenite with an approximately planar interface was observed to follow the parabolic behavior until ferrite can precipitate later inside the austenite part. Although this technique reduces the stereological and to lesser extent the crystallographic errors, the narrow temperature range at which measurements can be performed, is its main practical limitation. The measured parabolic rate constant at three temperatures for 0.21wt%C-1.52wt%Mn steel by means of this method are also represented in Figure 2-26.

2.3.2.2 Suitable thermodynamic treatment of Fe-C-i alloys

To model the kinetics of ferrite growth in ternary alloys, an appropriate thermodynamic description of the system, which sets the major boundary conditions of the simulation, first has to be selected. In contrast to binary Fe-C alloys, three different, well-quantified alternatives are available for alloyed steels, i.e. OE, PE and NPLE. Orthoequilibrium arises from the long-range redistribution of substitutional atoms inside the parent austenite, the state that is unlikely to be attained at the investigated temperature ranges for the above alloys. As also indicated in Table 2-3, the NPLE condition cannot be applied for all the growth temperatures, since the upper range of those temperatures lies outside the NPLE boundary. However, the entire measured data fall within the PE limit, which suggests PE is the only potential choice for the thermodynamic treatment of these systems.

To further evaluate the merit of either PE or NPLE as the thermodynamic treatment, particularly for the growth temperatures inside the NPLE limit, the predictions of the carbon diffusion model assuming either of these choices are compared with the experimental kinetics. Despite the fact that carbon contents of the examined alloys are relatively low, the diffusion model is chosen solely because it provides the upper limit for the ferrite growth rate, which corresponds to the prediction of the mixed-mode model if an infinite mobility is
assumed. The results of the analysis for ferrite growth are depicted in Figure 2-28 for the alloys containing 3.3wt%Ni and 1.52wt%Mn at temperatures of 665 and 730°C, respectively.

*Figure 2-28 Predictions of the diffusion model using different thermodynamic conditions for ferrite thickening in (a) 1.52wt%Mn alloy at 730°C and (b) 3.3wt%Ni alloy at 665°C.*

For the alloy containing Mn, the prediction based on the full local equilibrium at the interface to determine the interfacial carbon concentration is included as well for the sake of comparison only, since the associated local partitioning at the interface can be postulated, at
least in a formalistic way. It is evident that NPLE treatment gives rise to the kinetics which underpredicts the measured thickness, thereby it is definitely not a justifiable assumption. On the other hand, if PE description is employed; the model significantly overestimates the experimental data. However, the predictions can be potentially brought into accord with the measurements if a finite mobility for the interface is considered. Consequently, from the mentioned analyses it can be deduced that PE remains as the only viable choice for the thermodynamic treatment and is adopted in the following analysis.

It has to be noted that the growth rate decreases as the transformation proceeds, therefore the partitioning degree of substitutional atoms is expected to become more significant. However it is more relevant for the later stages of reaction, where growth is no longer parabolic in nature.

2.3.2.3 Prediction of mixed-mode model

Prior to considering the retarding effect of alloying elements, i.e. solute drag effect, it is imperative to evaluate the mobility term by which, in the framework of the mixed-mode model, the measured ferrite thickness in Fe-C-i alloys can be replicated. In other words, by employing the mobility as the only adjustable parameter, the predictions of the mixed-mode model are brought into agreement with the experimental data. The 3.3wt%Ni steel is selected for this analysis, since less tendency for solute-interface interaction compared to manganese containing steels has been reported [58]. Therefore, neglecting the probable solute drag effect is expected to cause minimal misinterpretation of the conclusion to be drawn.

The calculations of the mixed-mode model and the measured thickness of allotriomorphs as function of time for growth temperatures of 665, 680, 700 and 715°C are illustrated in Figure 2-29a to d, respectively.
Figure 2-29 Predictions of mixed-mode model and the experimental [94] growth of ferrite allotriomorphs for 0.12wt%C-3.3wt%Ni steel, intrinsic mobility is employed as the only fit parameter.

It is imperative to remark that the linear fit to the experimental data points does not go through the origin in some of the cases shown in Figure 2-29, i.e. they do not follow parabolic growth entirely. In this regard the mixed-mode model prediction, which deviates from parabolic growth at early stages, provides an adequate description of the reported kinetics. For each transformation temperature, the value for mobility was chosen such that
the best reasonable agreement with experimental data points could be achieved. Table 2-4 summarizes the mobility values obtained in this way expressed in units of the mobility proposed by Krielaart and van der Zwaag [72] for Fe-Mn alloys. In this scale the mobility varies from 2 to 0.11 when the growth temperature increases from 665 to 715°C indicating that the activation energy for mobility must be essentially different from that suggested for Fe-Mn systems. Presenting the mobility in an Arrhenius-plot as shown in Figure 2-30, the slope of this curve suggests a value of -271kJ/mol for the activation energy. Clearly a negative activation energy is inconsistent with the physical concept of thermally activated processes, the intrinsic mobility must increase with temperature and not decrease.

Table 2-4 The required values for the interface mobility (in terms of the ratio to Krielaart and van der Zwaag mobility, $M_{Fe-Mn}$) to replicate the measured thickening rate of Fe-0.12wt%C-3.3wt%Ni.

<table>
<thead>
<tr>
<th>$M_{fitted}/M_{Fe-Mn}$</th>
<th>2</th>
<th>1.2</th>
<th>0.7</th>
<th>0.11</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, °C</td>
<td>665</td>
<td>680</td>
<td>700</td>
<td>715</td>
</tr>
</tbody>
</table>

Figure 2-30 Arrhenius plot of fitted mobilities for 0.12wt%C-3.3wt%Ni resulting in an apparent activation energy of -271kJ/mol shows mobility would have to be decreased with increasing temperature.
2.3 Model Application

2.3.2.4 Implementing the solute drag effect

It is concluded from the preceding discussion that a simple mixed-mode model cannot provide a reasonable description of the experimental kinetics in Fe-C-i alloys, no matter how the problem is treated thermodynamically. Although to resolve this drawback, different remedies might be potentially employed, accounting for the retarding effect of solute-interface interaction is considered here. This so-called solute drag effect has been originally proposed as the prime reason for the observed discrepancies between the measured growth kinetics of ferrite and diffusion model predictions [62].

The amount of the required drag pressure to be employed in the mixed-mode model can be evaluated by means of the optimal fit to the experimental growth data as presented in the following.

2.3.2.5 Resulting solute drag parameters: Fe-0.21wt%C-1.52wt%Mn

The analysis of allotriomorph thickening in the 0.21wt%C-1.52wt%Mn alloy is first dealt with. As mentioned earlier, the drag pressure of segregated solute, here manganese, on ferrite-austenite interface can be quantified in terms of two prime parameters. For the diffusivity term an Arrhenius temperature dependency can be considered as is expressed by Equation 2-61. In this way the uncertainty associated with the assumed value for interface thickness is also embedded in the diffusivity parameter, which leads to minimizing the number of applied fitting parameters.

In the present work the activation energy is taken to be half of the one for austenite bulk diffusivity, i.e. 132kJ/mol and 137kJ/mol for Mn and Ni atoms [91], respectively. The pre-exponential factor, \( D_b/\delta \) is then adjusted such that \( D_b \) to be at least one order of magnitude larger than solute diffusivity in austenite. For given values of the diffusivity term, \( D_b/\delta \) and
mobility, $M$, the solute drag pressure which is required to replicate the experimentally observed kinetics can be found by employing an adequate binding energy $E_0$ as the third fitting parameter. Using the intrinsic mobility proposed by Krielaart and van der Zwaag, the solute drag parameters obtained from the optimal fit to the measured kinetics of ferrite growth in Fe-0.21 wt% C-1.52 wt% Mn are illustrated in Figure 2-31 for the three examined temperatures, i.e. 725, 730 and 735°C. To perform this simulation the $D_o/\delta$ ratio was changed from 30 to 1400 cm/s. By making reasonable assumption for $\delta$, i.e. 0.5 nm, the diffusivity across the interface can be expressed in units of the Mn diffusivity in austenite, therefore the above range corresponds approximately to a $D_o/D_{Mn}^\delta$ ratio of 60 to 1700. Obviously, various combinations of solute drag parameters, i.e. $E_0$ and $D_o/\delta$, can be selected to replicate the observed experimental kinetic data for each growth temperature. Further, the result suggests that stronger solute-interface interaction is required as transformation temperature increases.

![Figure 2-31 Effect of temperature on solute drag parameters to describe the experimental data [34] of ferrite plate thickening in Fe-0.21 wt pct C-1.52 wt pct Mn.](image)

Figure 2-31 Effect of temperature on solute drag parameters to describe the experimental data [34] of ferrite plate thickening in Fe-0.21 wt pct C-1.52 wt pct Mn.
As a rational outcome, it is expected that the intensity of the required solute drag effect does depend on the value selected for the interface mobility. In order to characterize the role of the mobility selection, the value of the Krielaart and van der Zwaag mobility was decreased and increased by a factor 0.3 and 3, respectively. The resulting solute drag parameters for the growth temperature of 725°C are depicted in Figure 2-32. Employing the mobility greater than that of Krielaart and van der Zwaag appears to have an insignificant influence on the required binding energy, while decreasing the mobility leads to a drastic drop in the resulting drag pressure. However, over the entire examined $D_o/D_M$ ratio and mobility range the binding energy is revealed to be within order of $RT$, which is consistent with the values reported in the literature [58,64].

![Figure 2-32](image)

*Figure 2-32 Effect of the selection of the intrinsic mobility on solute drag parameters to describe the experimental data [59] of ferrite allotriomorph thickening in Fe-0.21 wt pct C-1.52 wt pct Mn.*

### 2.3.2.6 Solute drag parameters: 0.12C-3.1Mn and 0.12C-3.3Ni(wt%) steels

Using the prescribed temperature dependencies for mobility and diffusivity terms, the combinations of the required solute drag parameters to describe the measured allotriomorph
2.3 Model Application

thickness in Fe-0.12C-3.1Mn and Fe-0.12C-3.3Ni(wt%) alloys for the range of investigated growth temperatures are presented in Figure 2-33 and Figure 2-34, respectively. To perform the simulations $M_0=5.8$ and 17.4 cm mol/Js were assumed for Mn and Ni containing system, respectively. As is evident in Figure 2-26 the growth of ferrite in 0.12C-3.3Ni(wt%) steel is much faster than that for Fe-0.12C-3.1Mn alloy for the entire investigated temperatures. Therefore in the framework of the mixed-mode approach, a larger $M_0$, i.e. 17.4 cm mol/Js was selected for the Ni-containing alloy. This is close to the minimum mobility that is required to replicated the thickening rate at 665°C, which corresponds to the temperature of the fastest growth rate in 0.12C-3.3Ni(wt%) steel (cf. Figure 2-26).

Consistent with the previous discussion, different sets of $E_o$ and $D_o/\delta$ values can be employed to describe the experimental data adequately. Moreover, a strong temperature dependency of the required binding energy is suggested. For example, assuming $D_o/\delta=710$ cm/s, $E_o$ increases from 0.75 to $3.7RT$ when temperature rises from 550 to 650°C in the 0.12wt%C-3.1wt%Mn steel. Taking the same value of $D_o/\delta$, the binding energy changes from 0.65 to $2.2RT$ in the Ni containing alloy when the temperature increases from 665 to 715°C. Also it is noted that manganese tends to show stronger interaction with ferrite-austenite interface compared to nickel.
2.3 Model Application

Figure 2-33 Solute drag parameters required to replicate the experimental growth kinetics [62] of ferrite at different temperatures in Fe-0.12wt%C-3.1wt%Mn.

Figure 2-34 Required solute drag parameters to describe the growth kinetics of ferrite measured [62] at different temperatures in Fe-0.12wt%C-3.3wt%Ni.
2.3.2.7 Discussion on the temperature dependence of binding energy

The present analysis of ferrite growth in the manganese containing alloys indicates that a binding energy of order of $RT$ is required for the model calculations to replicate the experimental kinetics. A binding energy of $RT$ is consistent with measurements of Mn segregation to austenite grain boundaries [88]. The alloy containing nickel shows less tendency for solute-interface interaction, this agrees with the expectation that Ni has a lower binding energy which is not more than about half of that of Mn [58,88]. However as an overall outcome it is apparent that stronger drag pressure of the segregated solute is required at the higher growth temperatures. The variation of binding energy with temperature, in terms of undercooling below $T_{Ae3}$, is compared for all the investigated alloys using $D_0/\delta = 710$ cm/s in Figure 2-35.

![Figure 2-35 Variation of applied binding energy with temperature to describe the experimental growth rate of ferrite [34,62] in 0.12wt%C-3.1wt%Mn, 0.12wt%C-3.3wt%Ni and 0.21wt%C-1.52wt%Mn steels.](image-url)
The predicted temperature dependence of the binding energy observed here is rather unexpected since according to the general concept of the solute-interface interaction, a temperature independent binding energy would be expected. It could be argued that it is simply an artifact resulting from the inappropriate temperature dependency which were assumed for the intrinsic mobility as well as for the solute diffusivity across the interface. Therefore, to exclude any potential impact caused by these two parameters, their activation energies have to be revisited.

First the role of the mobility term is considered by changing the assumed activation energy within an acceptable range, i.e. 140±40 kJ/mol in 0.12wt%C-3.1wt%Mn steel. Reducing the activation energy, $Q$ to 100kJ/mol leads to an $E_0$ that increases by $1.8RT$ per each 100°C increase in temperature. This temperature dependence of the binding energy is 20% less than that obtained by assuming the nominal value $Q=140$kJ/mol. Definitely, the effect due to changing the activation energy for the mobility is insufficient to eliminate the temperature dependence of binding energy.

The diffusivity of solute across the interface is the other unknown parameter for which, as first approximation, an activation energy, which is half of that for bulk diffusivity in austenite was assumed. Alternatively, postulating a temperature independent binding energy the activation energy $Q_0$ for the jump across the interface can be treated as an adjustable parameter. This is simply accomplished by using the data represented in the format of Figure 2-33 and Figure 2-34, i.e. the activation energy can be obtained by assuming a certain value for the binding energy, $E_0$. For example taking $E_0 =18$ and 28kJ/mol, respectively, the results of this analysis are summarized with an Arrhenius plot in Figure 2-36 for Fe-0.12wt%C-3.1wt%Mn. A similar plot assuming $E_0 =10$ and 15kJ/mol, respectively, for Fe-0.12wt%C-
3.3wt%Ni alloy is illustrated in Figure 2-37. The resulting negative apparent activation energies, i.e. approximately $-100\text{kJ/mol}$ and $-480\text{kJ/mol}$ for Mn and Ni containing alloys, respectively, indicate that this approach leads to an unreasonable behavior for the diffusivity of solute across the interface. Therefore, it can be ruled out that the increase of binding energy with temperature is an artifact of the selection of activation energies for mobility and diffusivity, respectively.

![Arrhenius plot for $D_b$ assuming constant values for the binding energy in Fe-0.12wt%C-3.1wt%Mn.](image)

Alternatively, the temperature dependency of $E_o$ might be explained by a gradual transition from paraequilibrium towards NPLE, i.e. the increase in the degree of solute partitioning in the vicinity of the interface as growth rate decreases at the later stages of ferrite formation. At the onset of transformation, sufficiently large thermodynamic driving pressure is available which gives rise to rather fast growth, such that no appreciable redistribution of substitutional elements is expected even locally at the ferrite-austenite interface. Therefore, the paraequilibrium assumption is a justifiable treatment at the beginning of growth. It is worth
to note that the deviation from paraequilibrium is likely to occur sooner at higher growth temperatures, where substitutional elements are more mobile and less driving pressure for allotriomorph thickening is available. Neglecting to account for this deviation from paraequilibrium could result in the overprediction of the experimental growth rates, which has to be compensated by considering a stronger solute-interface interaction, i.e. a temperature-dependent binding energy.

![Arrhenius plot for $D_b$ assuming constant values for the binding energy in Fe-0.12wt%C-3.3wt%Ni.](image)

*Figure 2-37 Arrhenius plot for $D_b$ assuming constant values for the binding energy in Fe-0.12wt%C-3.3wt%Ni.*

Apart from formation of a solute spike in front of the interface, at sufficiently high temperatures it is increasingly likely that the substitutional atoms may diffuse beyond the interface region. The extent of this redistribution is simply expected to exceed more than several times of the interface thickness. This is the concept that is proposed to be considered for rationalizing the aforementioned increase of the apparent binding energy.
2.3 Model Application

2.3.3 Analysis of the overall kinetics of ferrite formation in A36 steel

Although the kinetic analysis of allotriomorph thickening provides valuable insights into the underlying mechanisms of ferrite reaction and particularly aids to characterize the interfacial and solute drag parameters, it is of little industrial significance. In practical processing of low-carbon steels, austenite decomposes entirely to ferrite and some other phases, such that the assumption of planar geometry for the ferrite-austenite interface is no longer valid. Further, the applied cooling rates or undercooling is sufficiently large that nucleation site saturation at austenite grain boundaries is likely to occur promptly when less than 5 percent of ferrite forms. In these circumstances the overall kinetics can be accurately modeled by considering the subsequent growth of these ferrite particles provided that an appropriate geometry for the growing phase is assumed. Here, a spherical shape is adopted for the parent austenite grain that has a diameter replicating the mean volumetric austenite grain size. Ferrite constitutes the outer shell having uniform thickness circumferentially and grows toward the center of the spherical austenite grain.

2.3.3.1 Experimental kinetics

The examined material was chosen to be a model ternary steel with nominal composition of 0.17wt%C-0.74wt%Mn. The overall kinetics of ferrite formation during continuous cooling cycles had already been quantified in previous work at UBC [63]. However for the sake of completion, some selected isothermal and continuous cooling thermal treatments have also been conducted using the Gleeble 3500 thermomechanical simulator equipped with a dilatometer. Tubular samples of 8 mm outer diameter having a wall thickness of 1mm and a length of 20mm were employed in the transformation tests. The volume change during transformation is measured in terms of the change in diameter by means of a dilatometer.
attached on the outer surface of the sample right at its center plane, the same location where a thermocouple for temperature measurement is welded. The specimen is heated up employing resistance heating and cooled down with the help of forced convection by blowing helium gas through inside the tube. A precise computer-aided controller facilitates applying any complex thermal cycles readily. Special care has to be taken for isothermal cycles where the sample is subjected to high cooling rates after the austenitization stage, such that undershooting below the intended transformation temperature is prevented. The recorded kinetics can be substantially influenced by the amount of a potential temperature undershooting, even if it takes only a short time period. The details of the experimental procedure, as well as the practical method to interpret the acquired dilation data is delineated elsewhere [63,95]. The microstructure of the specimens was characterized by optical microscopy after sample preparation using traditional metallography procedures. The results can confirm if the employed thermal cycle yields to polygonal ferrite as the dominant structure. Further, the final ferrite fraction in either of iso- or non-isothermally treated specimens is quantified from optical micrographs.

Despite the more engineering relevance of continuous cooling ferrite formation, first the kinetics of isothermal austenite decomposition into ferrite is going to be analyzed here. The measured kinetics for transformation at four different temperatures 735, 745, 755 and 765°C from a prior austenite volumetric grain size of 96μm are illustrated in Figure 2-38. Using the lever law the dilation response recorded during isothermal ferrite formation was converted to ferrite fraction such that the plateau of the dilation curve at the end of reaction corresponds to the final fraction of ferrite predicted by paraequilibrium. As shown in Figure 2-39, the final fractions quantified from optical micrographs appear to be in an acceptable agreement with
both orthoequilibrium and paraequilibrium calculations, which are quite close for the investigated cases. Therefore, the experimental ferrite fractions at the end of reaction were normalized with respect to paraequilibrium predictions.

Figure 2-38 Measured kinetics of isothermal ferrite formation in a 0.17wt%C-0.74wt%Mn steel with an austenite of grain size of 96μm.

Figure 2-39 Measured and calculated ferrite fractions by optical metallography and the calculated ones assuming OE and PE.
2.3 Model Application

Typical microstructures at the end of isothermal austenite decomposition followed by quenching to room temperature are represented in Figure 2-40 for growth temperature of 735 and 765°C. These micrographs confirm that ferrite nucleates at austenite grain boundaries and grows with polygonal morphology.

![Microstructure of Fe-0.17wt%C-0.74wt%Mn specimens reacted isothermally](image)

*Figure 2-40 Microstructure of Fe-0.17wt%C-0.74wt%Mn specimens reacted isothermally at (a) 735 and (b) 765°C, d_f=96μm.*

2.3.3.2 Modeling the isothermal ferrite transformation

To replicate the above experimental growth kinetics, an attempt was first made to employ the mixed-mode model solely, without including the solute-interface interaction, i.e. the intrinsic mobility served as the only adjustable parameter for simulations. To calculate the required thermodynamic information, the system is treated under paraequilibrium condition. The fitting practices predicted smaller values for the mobility than that suggested for Fe-Mn by Krielaart and van der Zwaag. The mobility varies from 0.5 to 0.1 in unit of that for Fe-Mn when the transformation temperature increases from 735 to 765°C. The results are also
depicted in Table 2-5. The Arrhenius plot of this fitted mobility, i.e. the natural logarithm of mobility versus the reciprocal of temperature, suggests an apparent activation energy of \(-327\text{kJ/mol}\), which is not a sensible physical value for the thermally activated jump of atoms across the interface and indicates the mobility would have to decrease as temperature increases. This confirms again that in addition to the local reconstruction of BCC from FCC lattice at the transformation interface, another atomic process has to be in operation. Therefore solute-interface interaction seems to be a justifiable postulation here.

Table 2-5 The required values for the interface mobility (in terms of the ratio to Krielaart and van der Zwaag mobility, \(M_{\text{Fe-Mn}}\)) to describe the overall kinetics of isothermal ferrite formation in Fe-0.17wt%C-0.74wt%Mn.

| \(M_{\text{fitted}}/M_{\text{Fe-Mn}}\) | 0.5 | 0.35 | 0.2 | 0.1 |
| T, °C | 735 | 745 | 755 | 765 |

Thus, to model the isothermal kinetics of ferrite reaction in Fe-0.17wt%C-0.74wt%Mn alloy, the mixed-mode approach incorporating solute drag was employed. The ensuing result shown in Table 2-5, which suggests a mobility smaller than that of Krielaart and van der Zwaag would be sufficient to describe the isothermal ferrite kinetics for the transformation temperatures above 735°C. However, the analysis of ferrite formation during continuous cooling conditions, as will be discussed in the next section, revealed that a larger mobility is required for the lower transformation temperature down to 620°C, i.e. well below the temperature range studied in the isothermal test series.

Consequently, a mobility twice of that suggested for Fe-Mn is adopted for the calculations. This mobility would overpredict the measured kinetics if no retarding effect of solute atoms is accounted for. Then \(D_0/\delta\) and the binding energy, \(E_0\), serve as fitting parameters. It was
found that for $D_o/\delta = 142\text{cm/s}$ the optimal descriptions of the isothermal kinetics between 735 to 765°C can be achieved if the following temperature dependence for the binding energy is taken:

$$E_o (J/mol) = 41RT - 3.3 \times 10^5 \quad (2-64)$$

Adopting this binding energy implies that $E_o$ is in the order of RT, such that it increases from 1.1RT at 735°C to 2.3RT at 765°C. Further, the assumed $D_o/\delta$ of 142cm/s can be interpreted in terms of the $D_b/D_{Mn}$ ratio by taking a 1nm thickness for the interface, then $D_b/D_{Mn}$ varies from 270 at 735°C to 170 at 765°C, which as intended, yields to solute diffusivity across the interface to be at least two orders of magnitude larger than austenite bulk diffusivity. The model predictions using these adjustable parameters are plotted against the experimental overall kinetics in Figure 2-41. Apart from a slight overprediction at 765°C, the measured data are well captured using the present modeling methodology.

![Figure 2-41](image)

*Figure 2-41 Experimental (symbols) and calculated (solid lines) kinetics of isothermal ferrite formation in the temperature range of 735 to 765°C in Fe-0.17wt%C-0.74wt%Mn with an initial austenite grain size of 96μm.*
2.3 Model Application

2.3.3.3 Implication of the modified SD model to isothermal transformation

To quantify the drag effect of the segregated solute, the modified Purdy-Brechet theory was employed for all the simulations in the present work. The details of the refinements made to the original solute drag approach are elaborated in section 2.2.2.4. For ferrite formation at 735°C the variation of the solute drag pressure and the chemical driving pressure at the interface, with isothermal reaction time are represented in Figure 2-42. In case of employing the modified approach as shown in Figure 2-42a, both of these two energy terms, i.e. $\Delta G_{\text{int}}$ and $\Delta G_{\text{SD}}$, decrease monotonically and vanish entirely as transformation approaches to the end. In contrast, using the original solute drag model, as shown in Figure 2-42b, results in a non-zero drag pressure at the end of transformation, the point that is defined by a zero effective driving pressure at the interface.

In analysing the overall kinetics of isothermal ferrite evolution, the mentioned artifact enforces the growth to cease earlier, thereby the final fraction of ferrite is predicted to be substantially smaller than what experimental observation indicates. For instance Figure 2-43 shows the measured kinetics at 735°C together with the predictions of the mixed-mode approach using both the original and the modified solute drag model. Although incorporating the original Purdy-Brechet theory provides a decent agreement with experiments up to a ferrite fraction of 70%, the final fraction is significantly underestimated whereas the modified theory can capture the kinetics to final transformation stages. Attempting to assume a linear temperature variation for $E_o$, the observed premature cessation of growth is even more pronounced at higher transformation temperature because of the generally lower interface velocities.
Figure 2-42 Variation of thermodynamic driving pressure and solute drag pressure with time for growth of ferrite at 735°C in 0.17wt%C-0.74%Mn steel (a) using modified SD model, (b) adopting the original Purdy-Brechet quantification.
2.3 Model Application

2.3.3.4 Modeling the ferrite evolution during continuous cooling

As the prime benefit of developing a physically based model, it is expected that the model will be capable of capturing the situations beyond the cases where it was validated experimentally. Driven by this concept, attempts were made to apply the interfacial parameters which had been determined from the analyses of isothermal ferrite formation, to simulate the austenite decomposition into ferrite during non isothermal conditions in the same steel, i.e. Fe-0.17wt%C-0.74wt%Mn. The experimental kinetics for an initial austenite grain size of 18μm and the cooling rates of 1 and 16°C/s are examined, where polygonal ferrite was found to be the predominant microstructure. As illustrated in Figure 2-44, the model prediction is in good agreement with the measured kinetics. Capturing both isothermal and continuous cooling kinetics by employing a consistent set of adjustable parameters confirms the versatile capability of the proposed fundamental modeling approach.

Figure 2-43 Ferrite formation kinetics at 735°C in Fe-0.17 wt% C-0.74 wt%Mn showing the predictions adopting the original Purdy-Brechet solute drag theory and its modification, respectively.
2.3.4 Analysis of ferrite evolution in quaternary systems: DP and TRIP steels

The chemistry of advanced high strength steels is rather complex, containing more than one substitutional alloying element. This ensures the material to show the appropriate transformation characteristics during the industrial processing that it undergoes. In these multicomponent systems, the simultaneous segregation of different species to the ferrite-austenite interface is likely to occur. In these circumstances the subject of co-segregation becomes relevant and some attempts have been made to quantify this effect [67,68].

Undoubtedly, the observed apparent solute drag effect arises from the contribution of all segregated elements, which would have to be appropriately accounted for in a detailed fundamental model. However, to characterize the individual effects at least two physical properties, i.e. diffusivity across the interface and binding energy to the interface, would have to be introduced into the calculation for each alloying element. Noting that none of these
parameters are independently known from experimental or theoretical investigations, it is impractical to propose an overall transformation model which would incorporate all these parameters. Thus, in order to maintain a minimum number of unknown interfacial parameters, the drag effect of manganese is treated in the model as an effective force resulting from all segregated solute atoms. This assumption is based on the fact that manganese is the major alloying elements in all advanced high strength steels, i.e. usually in the 1.5 to 2wt% range. Then the activation energy of the diffusivity across the interface is taken as described for the Fe-C-Mn system and \( \Delta E \) represent the chemical potential difference of Mn across the interface which is affected by the presence of other substitutional elements, e.g. Mo or Si. Driven by this philosophy, the continuous cooling kinetics of ferrite formation in two novel dual-phase (DP) and TRIP steels, with composition of Fe-0.06wt%C-1.85wt%Mn-0.16wt%Mo and Fe-0.21wt%C-1.53wt%Mn-1.54wt%Si, respectively, have been analyzed. In both cases the simulation is restricted to the cooling conditions where polygonal ferrite is the predominant phase in the final microstructure.

The comparison of experimental data [96] with the model prediction is illustrated in Figure 2-45, for the DP steel with austenite grain sizes, \( d_y \), of 16 and 24\( \mu \)m, respectively. The adequate description of observed transformation kinetics is accomplished for two cooling rates of 1 and 18\( ^o \)C/s by selecting the mobility factor, \( M_0 \), as 10.5 cm mol/Js and setting \( D_0/\delta \) to 100 cm/s, while the binding energy is kept in the order of \( RT \) as given by:

\[
E_o (J/mol) = 1.5RT - 3.1 \times 10^{-3} \quad (2-65)
\]
2.3 Model Application

Figure 2-45 Measured [96] (symbols) and predicted (solid lines) kinetics of austenite decomposition into ferrite during continuous cooling of a dual-phase steel, Fe-0.06wt% C-1.85wt%Mn-0.16wt%Mo.

For the hot-rolled TRIP steel with prior austenite grain diameter of 20μm, the experimental data for the cooling rates of 1 and 5°C/s, where predominantly polygonal ferrite had been observed in the microstructure, were taken from literature [97]. Taking the mobility factor of 5.8cm mol/Js and assuming \( D_o/\delta \) as 28.4 cm/s, the model can accurately capture the measured kinetics. For the simulation, a linear temperature dependency for the binding energy was adopted, i.e.:

\[
E_o (J/mol) = 1.4RT - 2.4 \times 10^{-3} \tag{2-66}
\]

which is very similar to that obtained for the DP steel.
Figure 2-46 Comparison of observed data [97] and model prediction of ferrite formation kinetics during continuous cooling of TRIP steel, Fe-0.21C-1.53Mn-1.54Si (wt%), with an austenite grain diameter of 20μm.

Figure 2-47 and Figure 2-48 compare the solute drag parameters employed to perform the above simulations for DP and TRIP steels. Assuming an interface thickness, 2δ, of 1nm, manganese diffusivities across the interface are plotted for the entire temperature range of transformation. For the sake of comparison the diffusivity data considered for A36 steel is also included in Figure 2-47. Clearly these diffusivities are several orders of magnitude larger than the manganese bulk diffusivity in austenite. These results confirm that the diffusivity values used in the simulations are physically relevant and meaningful.

Further, as illustrated in Figure 2-48, the required binding energy of solute to the interface is in the order of RT for both steels in the examined temperature range and increases slightly with temperature. This is consistent with the previous findings for the Fe-C-Mn systems and also with that suggested in the literature regarding the interaction of alloying elements with moving ferrite-austenite interfaces [59,58,64].
Figure 2-47 Comparison of manganese diffusivity across ferrite-austenite interface for A36, DP and TRIP steels with bulk diffusivity in austenite, assuming $2\delta$ of 1nm.

Figure 2-48 Variation of manganese binding energy to $\alpha/\gamma$ interface with temperature for DP and TRIP steels.
2.4 Summary and Remarks (Ferrite Formation)

Relevant in particular to industrial processing conditions, a physically based model in the framework of the mixed-mode approach was developed to describe ferrite growth in multi-component steels. Assuming paraequilibrium, the kinetic effect of substitutional elements, which arises from the interaction of solute atoms with the migrating ferrite-austenite interface, was quantified using the modified Purdy-Brechet description. However, the transition from paraequilibrium to local equilibrium was not considered in the model.

The model employs three parameters, the intrinsic interface mobility, $M$, the binding energy of the major substitutional element to the interface $E_0$, and the diffusivity of this solute across the interface $D_b$, thus, the model has the same number of adjustable parameters as the traditional JMAK approach. In contrast to the JMAK methodology with entirely empirical parameters, the parameters employed in the proposed model are well defined in terms of their physics and the potential ranges of their values are well known. However, since the exact value of these parameters cannot be determined precisely by currently available experimental and/or modeling techniques, they have to be determined by the optimal description of the measured transformation kinetics. Analyzing different steel grades is then expected to provide a base guideline for selecting these parameters for new chemistries to be examined.

To verify the predictive capability of the model and also to further examine the physical relevance and temperature dependence of the model parameters, several isothermal and continuous cooling kinetics of ferrite formation were analyzed. The major findings and conclusions of the model applications are summarized here:

- The analysis of the thickening of ferrite allotriomorphs in three binary Fe-C alloys containing 0.11, 0.23 and 0.42wt%C revealed that the diffusion model overestimates
the experimental parabolic growth constants for the lower carbon contents, i.e. less than in 0.23wt%C. Assuming an interface mobility close to what was proposed by Krielaart and van der Zwaag, most of the measured thickening rates can reasonably be described by the mixed-mode model.

- Analyzing the kinetics of allotriomorph thickenings in 0.21wt%C-1.52wt%Mn, 0.12wt%C-3.1wt%Mn and 0.12wt%C-3.3wt%Ni steels, showed that various combinations of parameters, $E_o$ and $D_t$, can be employed to replicate the measured growth rate. Further, the ensuing solute drag parameters were found to hinge on the value selected for the mobility term.

- The overall kinetics of isothermal ferrite formation in a 0.17wt%C-0.74wt%Mn steel were described accurately by the model. Further, using the same interfacial parameters determined from the isothermal data, the model replicated reasonably the kinetics of ferrite evolution during continuous cooling treatments.

- Relevant to advanced high strength steels with complex chemistry, the continuous cooling ferrite formation of 0.06wt%C-1.85wt%Mn-0.16wt%Mo DP steel and 0.21wt%C-1.53wt%Mn-1.54wt%Si TRIP steel can also be described using the present model framework. Since for both cases Mn constitutes the major alloying element, its drag pressure was solely accounted for in the model. However, the ensuing values for solute drag parameters should be regarded as effective ones describing the apparent solute-interface-interaction of all the segregating species.

- Consistent with the literature, the determined binding energy was in the order of $RT$, however, a linear temperature dependency for $E_o$ was found here for all examined cases. This can potentially be related to the increase of the partitioning degree of
substitutional atoms at higher temperatures and further investigation of this phenomenon is required.
Chapter 3: Bainite Transformation

3.1 Introduction

Apart from the diverse characteristics of bainite, in terms of both kinetics and morphological appearance that renders this area of research to be an active one for further explorations, bainite transformation has recently gained more attention due to its significance in processing of newly-developed advanced high-strength steels. In particular the bainite reaction is a crucial processing step for TRIP steels during which stabilization of untransformed austenite is accomplished. Further, in processing of DP steels formation of bainite upon cooling from intercritical region has to be prevented. This constitutes the motivation behind the research outlined in the present chapter.

The underlying mechanism of the bainite reaction has been a matter of debate for many years [98, 99,100,101]. In the case of TRIP steels, the issue becomes even more complex since bainite formation occurs from very small austenite grains, i.e. 1-3μm, encompassed by a ferrite matrix. Moreover, due to presence of silicon, aluminum or other suitable alloying elements the formation of carbides is delayed. As a result, carbide-free bainite morphologies develop which adds further controversy to the subject [102,103].

The aim of this chapter is to better understand the features of bainite formation in the alloying system that was originally developed for classical TRIP steels. Moreover, the focus is to develop a model that is applicable to the bainite reaction in TRIP steels. As a first step, the austenite-to-bainite transformation is investigated in a 0.6C-1.5Mn-1.5Si (wt%) steel, i.e. for the chemistry expected at the beginning of the bainite treatment in a classical 0.2C-1.5Mn-1.5Si TRIP steel (cf. points 2 and 3 in Figure 1-1). The isothermal transformation
kinetics are analyzed using available modeling approaches, i.e. Johnson-Mehl-Avrami-Kolmogorov (JMAK), as well as diffusional [104,22] and displacive [23] methodologies. The capabilities and limitations of these approaches are examined in regard of capturing the experimental kinetics. In the second part, the kinetics and microstructural features of bainite evolution after intercritical treatment of a classical TRIP steel, i.e. 0.18C-1.55wt%Mn-1.70wt%Si, is explored. Finally, regarding transformation during continuous cooling treatments for a Mo-TRIP steel with 0.19wt%C-1.5wt%Mn-1.6wt%Si-0.2wt%Mo, the kinetics of bainite evolution after ferrite formation is studied.

3.2 Literature Review

3.2.1 Overview

Bainite is a product of austenite decomposition in the temperature gap between the region at which the products are formed by a diffusional mechanism, e.g. pearlite or polygonal ferrite, and by a displacive mechanism, i.e. martensite region. The reason that at sufficiently low temperature below $A_{c1}$, bainite competes with pearlite formation is attributed to the asymmetry of the phase diagram [105], i.e. the extrapolated $A_{cm}$ line is much steeper than the extrapolation of $A_{c3}$ line. This gives rise to the preference of separate formation of ferrite plates rather than lamellar-cooperative growth of ferrite and cementite. However as the temperature is lowered further, then enough driving pressure to overcome the strain energy associated with the diffusionless formation of supersaturated bct ferrite, i.e. martensite, would be provided and austenite transforms athermally to martensite. The start temperature of bainite transformation depends on steel chemistry and can be represented by the following empirical equation [106]:

\[
T_{start} = T_0 - \frac{1}{K}
\]
From the microstructural point of view, although bainite features quite diverse morphologies depending on the alloying system and reaction temperature \[107,108\] it is traditionally defined as a fine aggregate of ferrite plates (or laths) and cementite particles precipitated between or within the ferritic counterpart. These two distinct types of morphology are referred to as upper and lower bainite, respectively. The carbides that appear as coarse particles between two adjacent laths are called interlath carbides, and these precipitate in form of fine discs within each lath at the \((112)_{BF}\) plane are known as intralath. It is common to refer to the ferritic part of bainite as bainitic ferrite (BF), which is quite different from polygonal ferrite. Bainitic ferrite has a very high dislocation density of about \(10^{14} \text{m}^{-2}\), and has a lath or plate morphology. Figure 3-1 shows the three-dimensional view of lath and plate, respectively.

![Figure 3-1 3D representation of lath and plate \[109\].](image)

### 3.2.2 Mechanism of bainite transformation

Due to the complex characteristics of bainite evolution, which has led to conflicting observations and interpretations, no conclusive description regarding the underlying physics of this reaction has been provided yet. Adopting shear mode formation of bainite as
originally suggested by Zener [104], Bhadeshia has divided the decomposition of austenite into two categories, "Displacive" and "Reconstructive" [109]. The former is characterized by invariant-plane strain shape change featuring a large shear component in which neither iron nor substitutional atoms can migrate individually. In case of the reconstructive transformation, a new lattice is constructed by diffusion of iron and substitutional atoms, as well as the interstitial species during both nucleation and growth events. In this approach, Widmanstätten ferrite, bainite and martensite fall in the displacive category, although different growth criteria have to be fulfilled for each to be evolved [109]. On the other side of this long lasting dispute, several researchers are arguing for diffusional edgewise growth of bainite, which in some cases is suggested to be controlled by a ledge mechanism [99], and regarded bainitic ferrite essentially to be the same as a Widmanstätten plate. A brief review of both approaches is provided in the following.

3.2.3 **Displacive mechanism of bainite transformation**

According to the displacive mechanism of bainite formation as described in detail by Bhadeshia [109], the transformation has a shear nature and resembles the martensite transformation. At sufficiently high under cooling, when diffusional transformation of ferrite or pearlite becomes impossible, sufficient driving pressure for diffusionless, shear mode transformation becomes available. At this condition, bainitic ferrite laths (or platelets) nucleate at austenite grain boundaries and grow to a certain limited size, without any carbon diffusion. The change in crystal structure of the substitutional sublattice, which occurs during diffusionless growth, has a large shear component that gives rise to the observation of a surface relief effect. If the strain is elastically accommodated, then the strain energy of
bainitic ferrite amounts to about 400Jmol\(^{-1}\). Some of the shear strain due to shape change is accommodated plastically by slip in both parent austenite and product ferrite. The dislocation debris in austenite, created by plastic accommodation (or plastic relaxation) stifles further growth of bainitic ferrite laths. Thereby they grow to a limited size, much smaller than the austenite grain size. Transformation proceeds by successive nucleation of new laths, face-to-face near the tip of already existing laths, and subsequent growth. The aggregate of these parallel laths is known as a sheaf or packet of bainite. The subunits within a sheaf have small relative misorientations but they all exhibit the same variant of parent-matrix orientation relation. This sub-structural feature of a bainite plate, i.e. consisting of several subunits detected only by TEM technique, is an inherent characteristic that discriminates bainitic ferrite from Widmanstätten ferrite.

The supersaturation of bainitic ferrite with respect to carbon constitutes the central basis of displacive growth, after which the excess carbon is soon partitioned into the adjacent residual austenite, encompassed by BF laths. The thickness of interlath residual austenite is very small, so that their carbon enrichment takes place only in few milliseconds. As transformation proceeds, carbon accumulates in untransformed austenite until the diffusionless growth of newly nucleated laths becomes thermodynamically impossible. At this stage (the so-called transformation stasis) further transformation ceases, which is the basis of the "incomplete reaction" theory of bainite. The maximum extent to which bainite reaction can proceed is determined by the \(T_o\) line, which represent the final limit of austenite enrichment with carbon before the diffusionless growth ceases. Actually, the \(T_o\) line is the locus point where austenite and ferrite with the same chemistry have equal free energies. Figure 3-2(a) illustrates the free energy curve for austenite and ferrite and the definition of...
the $T_0$ line, and Figure 3-2(b) shows the location of the $T_0$ line in the Fe-C diagram. To account for the strain energy term the $T_0$ line is modified to a $T'_0$ line.

![Figure 3-2](image)

**Figure 3-2** The $T_0$ line, (a) The free energy curves of austenite and ferrite and their relation to the different phase boundaries in the Fe-C diagram, (b) the relative location of $T_0$ in the Fe-C diagram [109].

### 3.2.4 Carbide precipitation

When the initial carbon concentration is sufficiently high and elements such as Al or Si are not present, the conditions for carbide precipitation from enriched austenite, trapped between ferrite platelets may be satisfied. Therefore, if the carbon concentration of residual austenite, $c_r$, exceeds the amount which is given by extrapolation of the $\gamma/(\gamma+\text{cementite})$ boundary in the Fe-C phase diagram, the carbide precipitation from enriched austenite takes place. The shaded area in Figure 3-2(b) shows the region where the austenite is unstable with respect to cementite and its decomposition occurs. Note that below the critical temperature $T_c$, carbide precipitation from austenite occurs simultaneously with the growth of bainitic ferrite laths.

At sufficiently low temperature, when due to low mobility the time to decarburize supersaturated BF platelet is larger than the time required to precipitate cementite within the
3.2 Literature Review

Chapter 3

platelet, the latter process precedes the carbon rejection to adjacent austenite and intralath carbides would form. It has been reported that in plain Fe-C alloys, more than 0.3% carbon is necessary to fulfill this condition. As a consequence of carbide precipitation within platelets, some carbon is already tied up in the form of cementite. Therefore, precipitation of cementite from enriched austenite is reduced.

If the initial carbon content is very low, e.g. ultra-low carbon bainitic (ULCB) steels, or graphite-former elements such as Si and Al are present, carbide formation can be inhibited or lags behind BF formation for a long period of time. The resulting morphology is referred to as carbide-free bainite. In TRIP steels, carbide-free bainite is required to guarantee sufficient carbon enrichment in austenite in order to shift the martensite start temperature below room temperature. The effect of silicon is associated with its low solubility in cementite [110]. Therefore, the need for silicon to diffuse away from the cementite/ferrite interface could explain its retardation effect on cementite growth. Figure 3-3 shows the three different cases for bainite: carbide free bainite, upper bainite and lower bainite.

![Figure 3-3 Evolution of three different bainite morphologies from the supersaturated plate](image)

*Figure 3-3 Evolution of three different bainite morphologies from the supersaturated plate [109].*
3.2 Literature Review

3.2.5 Thermodynamic criteria for displacive nucleation and growth

According to the displacive theory [109], a sheaf of bainite consists of many ferrite subunits formed by a shear mechanism and grow to a certain size. Autocatalytic nucleation, in which new subunits nucleate near the tip of an already existing one, is a key factor in formation of a sheaf. The nucleation process is displacive [111] in which similar to martensite nucleation the activation energy of nucleation varies linearly with the chemical driving pressure [112], in contrast to classical nucleation theory that predicts inverse proportionality to the square of driving pressure. The linear dependence arises from the idea that many preexisting embryos are available in the undercooled austenite. Therefore, the activation energy is then a barrier to interface migration. It is suggested that glissile dislocation located in the austenite grain boundaries can dissociate directly into an embryo of ferrite at sufficiently high driving pressure.

Nucleation takes place with carbon partitioning under paraequilibrium condition [111]. The minimum driving pressure required to initiate the displacive nucleation, $G_N$, is found to be a linear function of the transformation start temperature for bainite, $T_S$ [113]. A universal nucleation function for $G_N$ has been proposed that predicts the highest temperature at which ferrite can nucleate by displacive mechanism, irrespective of alloy chemistry. This universal function, which is a criterion for displacive nucleation, is given by [113]:

$$G_N (J/mol) = 3.647T_S - 2540 \tag{3-2}$$

This equation can be applied to either bainitic or Widmanstätten ferrite since their nucleation process is suggested to be similar in nature. However, different growth criteria have to be fulfilled that the nuclei can grow into a Widmanstätten or bainite plate as outlined below.
Displacive growth of bainite plates occurs through an interface-controlled mechanism and involves full carbon supersaturation. Bainite subunits do not seem to grow in a mutually accommodating manner unlike the growth of Widmanstätten plates, so that the resulting surface relief does not represent a tent shape [111]. The motion of the interface is soon terminated by an accumulating friction stress. Indeed, the dislocation debris created by plastic accommodation stifles further growth of ferrite plates. The proposed stored strain energy associated with the formation of bainitic ferrite is 400 J/mol. Therefore, the growth criterion can be expressed as [111]:

$$\Delta G^{y \rightarrow a} \leq -400 \text{ Jmol}^{-1}$$  \hspace{1cm} (3-3)

where, $\Delta G^{y \rightarrow a}$ is the driving pressure for composition invariant transformation of austenite to supersaturated ferrite, i.e. without compositional change. Graphical representation of this equation is the $T'_o$ line in the phase diagram by which the maximum carbon content of remaining austenite can be evaluated (see Figure 3-2).

Similarly, for Widmanstätten ferrite the growth criterion is suggested as [113]:

$$\Delta G^{y' \rightarrow y' + a} \leq -50 \text{ Jmol}^{-1}$$  \hspace{1cm} (3-4)

where, $\Delta G^{y' \rightarrow y' + a}$ indicates the free energy change accompanying the ferrite formation with paraequilibrium carbon content, i.e. with carbon partitioning.

Although both Widmanstätten and bainitic ferrite are proposed to evolve with a displacive transformation mechanism [109], carbon partitioning is assumed for their nucleation stage. This seems to degrade the self-consistency of the displacive philosophy.
3.2 Literature Review

3.2.6 Displacive model to predict the overall kinetics of bainite

Rees and Bhadeshia [23] proposed a nucleation-based model that transformation proceeds by displacive autocatalytic nucleation of ferrite subunits. The growth rate of subunits is so high that at the moment of nucleation they can grow to a certain size promptly. The incremental change of volume fraction of bainite due to nucleation of ferrite subunits between $t$ and $dt$ is given by:

$$df_B = (1 - f_B) u \dot{I} dt$$  \hspace{1cm} (3-5)

where $f$ is the actual volume fraction of bainite, $\dot{I}$ is the nucleation rate per unit of volume and $u$ is the volume of a subunit.

The main underlying assumptions considered in this model can be summarized as follows:

( I ) Carbide precipitation is absent due to presence of silicon.
( II ) Activation energy of displacive nucleation is directly proportional to driving pressure for transformation, consistent with martensite nucleation. Therefore, the volumetric nucleation rate at austenite grain boundaries, $\dot{I}_o$ is given by:

$$\dot{I}_o = k_i \exp \left[ \frac{-K_2}{RT} (1 - \frac{\Delta G_m}{r}) \right]$$  \hspace{1cm} (3-6)

where, $k_i$ is the nucleation rate at the Widmanstätten ferrite start temperature $W_s$, $\Delta G_m$ is the driving pressure for bainite formation, $r$ and $K_2$ are constants, and $R$ and $T$ have their usual meaning. The displacive nucleation rate at $W_s$ is identical for all steels [113].

The minimum driving pressure for bainite transformation at $W_s$ is $G_N$, referred to the universal nucleation function, i.e. Equation (3-2). Indeed, $G_N$ is the minimum driving pressure required for displacive nucleation of ferrite at the bainite start temperature, $B_S$, which is defined as the highest temperature where bainite formation can be detected.
experimentally during continuous cooling of the examined steel. Alternatively, $B_S$ can be estimated from empirical expressions such as the Steven-Haynes equation [106].

(III) Carbon enrichment of the remaining austenite that affects the nucleation rate is taken into account. Partitioning the excess carbon of ferrite subunits soon after their growth increases the carbon content of adjacent parent austenite, which induces a drop in $\Delta G_m$. If the driving pressure is assumed to vary linearly with the extent of the reaction, i.e. $f_B$, between its initial value $\Delta G^{\gamma\rightarrow\gamma+\alpha}$ and its final value $G_N$ (since below $G_N$ no displacive nucleation is permitted), then:

$$\Delta G_m = \Delta G^{\gamma\rightarrow\gamma+\alpha} - f_B (\Delta G^{\gamma\rightarrow\gamma+\alpha} - G_N) \quad (3-7)$$

(IV) The effect of autocatalysis, i.e. the increase in number of nucleation sites as volume fraction of bainite increases, is taken into account as:

$$\dot{\tilde{i}} = \dot{i}_0 (1 + f_B \beta \theta_B) \quad (3-8)$$

where $\dot{i}$ is the effective nucleation rate, $\theta_B$ is the maximum fraction of bainite, and $\beta$ is the autocatalysis factor. However, due to carbon built up at the $\alpha/\gamma$ interface, a temporary local decrease in driving pressure takes place, hence the autocatalysis factor $\beta$ should be related to the mean carbon concentration of austenite $\bar{x}$, as:

$$\beta = \lambda_1 (1 - \lambda_2 \bar{x}) \quad (3-9)$$

where, $\lambda_1$ and $\lambda_2$ are empirical constants.

(V) Effect of austenite grain size, $d_\gamma$ on nucleation rate, is assumed to be proportional to $k'd_\gamma$, where $k'$ is an empirical constant.

The final equation for transformation kinetics that includes all of the above assumptions is given by:
The solution of Equation 3-10, gives the time $t$, taken to form a certain volume fraction of bainite $f_B$, at the given reaction temperature.

It is worthwhile to delineate more the significance of the adjustable parameters used in the displacive approach. The parameter $K_1$ describes the role of austenite grain size and the volume of subunit is included. Further, parameter $K_2$ dictates to which degree the nucleation rate is affected by the thermodynamic driving pressure, for instance setting $K_2$ to zero or a sufficiently small value (<200J/mol) results in a nucleation rate which is independent of the calculated value for the driving pressure. The values reported by Rees and Bhadeshia for the three adjustable parameters (i.e. $K_1$, $K_2$, $\beta$) quantified from fitting to a large number of experimental data in Fe-C-Mn-Si steels are given in Table 3-1. By using different sets of experimental data, quite different parameter combinations were proposed. Using an initial set of well defined data, parameter values were found which were, in particular for $K_2$ and $\beta$, significantly different than those for other steels analyzed. Most notably the value for $K_2$ is sufficiently small for this set of bainite transformations in Fe-C-Mn-Si that the nucleation rate becomes independent of the driving pressure. Including additional data, the parameter combination is also for the Fe-C-Mn-Si system similar to that for other steels and $K_2$ is now sufficiently large that the model becomes sensitive to the actual driving pressure. In summary, reviewing the analysis of Rees and Bhadeshia indicates that application of the
model is very sensitive to the data base employed and even the order of magnitude of the adjustable parameters is still not very well established.

Table 3-1 Reported values for adjustable parameters based on the best fit for Fe-C-Mn-Si alloys [23].

<table>
<thead>
<tr>
<th></th>
<th>$K_1$, m$^{-3}$s$^{-1}$</th>
<th>$K_2$, J/mol</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generic values reported for Fe-C-Mn-Si alloys (initial data set)</td>
<td>$2.6 \times 10^{-8}/d_\gamma$</td>
<td>1.925</td>
<td>4.756</td>
</tr>
<tr>
<td>Generic values reported for Fe-C-Mn-Si alloys (extended data set)</td>
<td>$5.2 \times 10^{-8}/d_\gamma$</td>
<td>$6.395 \times 10^3$</td>
<td>9.696</td>
</tr>
</tbody>
</table>

In the aforementioned approach a number of crucial physical events, such as autocatalytic nucleation and the carbon enrichment of the untransformed austenite, were treated in a crude manner. More recently, some of these drawbacks pertinent to the original model were addressed by Matsuda and Bhadeshia [114]. The main improvement seems to be discriminating between grain boundary and autocatalytic nucleation through explicit quantification of each contribution. In the initial stage of the reaction grain boundary nucleation is assumed to govern the overall kinetics, whereas the evolution of sheaves contributes to the further increase of the bainite fraction later on. The growth of a bainite sheaf is intermittent in nature controlled by autocatalytic nucleation of its constituents, i.e. subunits. By adopting the concept of extended area developed by Cahn [115], the transformed area on a certain test plane parallel to the grain boundary can be translated into the incremental bainite fraction. Then a more realistic description of the rate equation for bainite evolution was defined. It has to be noted that the intersection of growing sheaves nucleated at different time scales with a test plane constitutes the transformed area on the plane under consideration.
3.2 Literature Review

The temperature dependence of bainite plate thickness is implemented in the revised model as well. Moreover, the carbon content in the untransformed austenite is updated at each time step. Overall, although a more complex numerical scheme is associated with the revised model, it benefits from more realistic physics compared to the original approach, yet its predictive capability has to be examined and still its applicability is confined to carbide-free bainite.

3.2.7 Diffusional theory of bainite formation

This idea is originated on microscopic observations performed by Hultgren [116], who proposed that bainite forms by diffusion controlled edgewise growth of a set of parallel Widmanstätten plates of ferrite followed by precipitation of cementite in the inter-plate regions. Carbide precipitation increases the growth rate of ferrite plates by up to three times [117] compared to the cases where cementite formation is suppressed by the presence of Si or Al. Bainitic ferrite grows at a constant rate and without carbon supersaturation, i.e. with a carbon content according to the extrapolation of the $\alpha/\alpha+\gamma$ phase boundaries. However, the capillary effect, interface reaction and interaction of segregating solutes with the interface, can potentially alter the interfacial conditions under which ferrite plates evolve.

The proponents of this school of thought based on detailed TEM studies [118,119] are in firm believe that the interfacial structure of the broad face between ferrite plates and the austenite matrix is incapable of motion by glide, the feature that is essential for displacive type of growth. It has been observed that the interface consists of a single set of misfit dislocation and a set of structural ledges [118], which are formed due to energy minimization and provide an optimized match between the associated phases. The height of these structural
ledges was observed to be of a few atomic distances and is expected to be completely sessile. Aaronson and Kinsman [98], who argued against displacive growth of bainite, proposed that the tip of bainite plates comprises an array of growth ledges. Therefore, it is necessary to consider the plate lengthening in terms of the diffusion controlled ledge mechanism in which no atom attachment is allowed on the trace of a ledge and interface can only move by lateral migration of ledges.

From a kinetic point of view, the experimental measurements of edgewise growth [120] did not reveal any abrupt change of lengthening rate as the reaction temperature was lowered from 700 to 380°C and even further down to 230°C [117], indicating that the growth mechanism of Widmanstätten and bainitic ferrite are essentially similar [120].

The fundamental similarity in the growth mode of Widmanstätten ferrite and bainitic ferrite was also supported by Hillert [22], who modified an equation proposed by Zener [104] for diffusion controlled edgewise growth of a plate precipitate surrounded by a disordered interface. The modified equation, which utilized the thermodynamic data given by a simple linear extrapolation of phase boundaries to lower temperatures, was successfully applied to the kinetics of Widmanstätten and bainitic ferrite [22]. However, he suggested that the lower growth rates experimentally observed as compared to the model predictions could be attributed to some resistance in interface motion that must be overcome.

The displacive theory of bainite formation in part relies on some other experimental observations, e.g. high defect densities in bainitic ferrite, surface relief effect and transformation stasis. These issues were tried to be addressed as well by the proponents of the diffusional theory. Bainitic ferrite has a high dislocation density that increases as transformation temperature decreases. These types of defects that are left behind the
transformation interface are referred to as the *trailing effect* [119]. According to the diffusional thought, the occurrence of dislocation substructure can be ascribed to a normal migration mode of the ledges, which becomes possible at sufficiently high driving pressures [101]. This mode of migration induces high defect densities in the product phase. The ledges are usually expected to grow through lateral migration at intermediate undercoolings. Further, it is argued [119] that if bainite would form by a shear mechanism it is definitely expected to observe twins as another type of trailing defects, which can potentially be formed in higher carbon austenite or when the matrix is subjected to hydrostatic pressure. The lack of twin evolution is regarded as further support for the diffusional argument.

The emergence of the surface relief was originally examined by Ko and Cottrell [121] in 1942 who discovered that acicular ferrite features a surface effect similar to that of martensite. According to this finding and with respect to not very fast lengthening rate, they concluded that ferrite plates grow at the rate controlled by carbon diffusion in austenite while the substitutioanal sublattice may transform by martensite-like shear mechanism.

The issue of transformation stasis, in the framework of the diffusional approach, was attributed to the role of plastic accommodation in austenite [103]. Assuming the shape change associated with formation of bainitic ferrite has a pure dilatational nature, at least on the macro-scale, and is plastically accommodated solely in the untransformed austenite, a crude quantification for the dissipation of Gibbs energy due to this plastic work was provided. The onset of transformation stasis can then be defined when the energy release due to the diffusional formation of ferrite from supersaturated austenite becomes equal to the energy loss as result of the aforementioned plastic accommodation. Employing this criterion,
the carbon content of the untransformed austenite at the stasis was shown to decrease with
growth temperature and increase with the initial carbon concentration of the alloy.

Further, it is shown that the transformation stasis is not a unique feature of bainite formation
in Si and Al containing steels, it also can be observed in alloys with strong carbide formers
such as Mo [122] and Cr [123]. It was found that the measured maximum fraction of bainite
during isothermal holding depends on the alloying content of initial austenite, the
pronounced effect that cannot be explained solely by thermodynamic considerations in terms
of shifting the equilibrium boundaries, for instance $T_0$ line which is invoked to define the
limit of displacive growth [109]. In these circumstances, the premature growth cessation
might be attributed to solute-interface interaction. For example Reynolds et al. [122]
explained the stasis in terms of both nucleation and growth of bainite subunits based on the
extensive experimental characterization of the transformation stasis in a series of high purity
Fe-C-Mo steels containing 0.06 to 0.27wt%C and 0.23 to 4.28wt%Mo. They proposed that
the simultaneous suppression of sympathetic nucleation and the restriction of growth yield to
this phenomenon. Further, the growth cessation was considered to be due to the drag effect of
molybdenum on the ferrite-austenite interface.

3.2.8 Mathematical expression for growth kinetics of a plate

The edgewise growth rate, $v^g$, of a growing plate, e.g. bainitic plate, with a radius $\rho$ of
curvature which is controlled by carbon diffusion away from the advancing disordered tip
was originally discussed by Zener [104]. Based on the dimensional argument, he proposed an
equation for steady state growth velocity, which was later modified by Hillert [22] in order to
be applicable to parent phases with high degree of supersaturation, as given by:
\[ v^g = \frac{1}{2\rho} \frac{X^\gamma_o - X_o}{X^\gamma_o} D^\gamma_c \] (3-12)

where \( X_o \) is the initial carbon content of parent austenite and \( X^\gamma_o \) is the modified equilibrium carbon concentration along the tip of \( \alpha/\gamma \) interface to account for the surface energy term \( V_m \sigma_{\alpha\gamma}/\rho \). Plate shape is assumed to be cylindrical featuring circular tip and the concentration is constant along the tip. Originally, to assess the supersaturation term as a function of tip curvature, i.e. \( X^\gamma\rho - X_o \), Zener proposed to assume a dilute solution for the matrix and to consider the following replacement using the equilibrium interfacial concentration:

\[ X^\gamma\rho - X_o = (X^\gamma_{eq} - X_o)(1 - \frac{\rho_c}{\rho}) \] (3-13)

where \( \rho_c \) is the critical tip curvature at which the entire chemical driving pressure is exhausted by the interfacial energy, i.e. growth would stop.

Horvay and Cahn [124] treated the plate as elliptical paraboloid and considered constant concentration along the plate interface. An exact solution to the diffusion problem of a growing cylindrical plate featuring a parabolic tip was first presented by Ivantsov [125], i.e.:

\[ (\pi p)^{0.5} \exp(p) \text{erfc}(p^{0.5}) = \Omega_o \] (3-14)

where the left side of the expression, \( I(p) \), is a function of the Peclet number, \( p=(v^\beta \rho/2D) \) and \( \Omega_o \) denotes the supersaturation with respect to the equilibrium concentrations:

\[ \Omega_o = \frac{X^\gamma_{eq} - X_o}{X^\gamma_{eq} - X^\alpha_{eq}} \] (3-15)
In Ivantsov’s treatment the role of tip curvature on the interfacial concentration of solute is neglected, however adopting Zener’s simplification one can simply multiply the equilibrium supersaturation, \(Q_0\), by \((1-\rho_c/\rho)\), to account for the capillary effect.

Trivedi [126] adopted Ivantsov’s solution and improved it to capture the effect of capillarity and interface reaction kinetics on the local interface concentration for a plate with parabolic cylinder geometry. A simplified version of this model was proposed by Bronze and Trivedi [127]. As discussed recently by Hillert et al [128], Trivedi’s description is only valid for a high amount of equilibrium supersaturation, i.e. \(Q_o > 0.5\) and further it does not provide any solution below a certain radius of curvature.

Quidort and Brechet [117] have recently employed this simplified equation to model the growth kinetics of upper bainite plates in low alloy steels. They measured the longest plate observed by optical/scanning electron microscope and found linear lengthening rate of plates that was in accord with the model prediction. The slower growth rates observed are attributed to a solute drag effect, which is not incorporated into their model.

Enomoto [129] presented an informative comparison of these various models for edgewise lengthening of ferrite plate, which is reproduced in Table 3-2 with some additional remarks. The kinetic model based on ledgewise growth, which has been developed by Atkinson [130], is also included in this comparison.
### Table 3-2 Models of plate-lengthening rate [129].

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Year</th>
<th>Plate Geometry</th>
<th>Boundary Condition</th>
<th>Remarks/drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ivantsov</td>
<td>1947</td>
<td>Cylindrical with parabolic tip</td>
<td>Constant concentration</td>
<td>No capillary effect considered</td>
</tr>
<tr>
<td>Zener-Hillert</td>
<td>1957</td>
<td>Cylindrical with circular tip</td>
<td>Constant concentration along the tip</td>
<td>Dilute solution for matrix, maximum growth rate always at $\rho_c/\rho = 2$</td>
</tr>
<tr>
<td>Horvay-Cahn</td>
<td>1960</td>
<td>Tip of elliptical paraboloid ($\rho_r/\rho = 0$)</td>
<td>Constant concentration</td>
<td></td>
</tr>
<tr>
<td>Trivedi</td>
<td>1970</td>
<td>Cylindrical with a parabolic tip</td>
<td>Concentration varies with curvature and interface reaction kinetics</td>
<td>Dilute solution approximation. Valid for moderate to high supersaturation, $\rho_c/\rho$ corresponds to maximum growth rate changes with the degree of supersaturation</td>
</tr>
<tr>
<td>Atkinson</td>
<td>1981</td>
<td>Ledge</td>
<td>No concentration gradient along the riser, no flux on the terrace</td>
<td></td>
</tr>
</tbody>
</table>
3.2 Literature Review

3.2.9 Evaluation of bainite transformation kinetics

Adopting the Zener-Hillert [22] growth equation, Minote et al. [131] employed a diffusional model to predict the overall kinetics of bainitic ferrite formation in a classical TRIP steel, i.e. Fe-0.2C-1.5Mn-1.5Si (wt%). In addition, they adopted the displacive approach of bainite formation [23] for modeling the overall kinetics. They observed that the experimental kinetics of bainite transformation above 350°C is in accord with the predictions of the diffusional mechanism, while it is consistent with the calculations of the displacive model below 350°C, as shown in Figure 3-4. Note that at 350°C, both models give similar predictions, which are in good agreement with the experiments.

![Figure 3-4](image)

*Figure 3-4 The change in volume fraction of bainite during austempering at different temperatures. Solid and dotted curves show calculated data based on the diffusional and displacive model, respectively [131]*

The displacive approach is a nucleation controlled model and does not present any estimation of subunit growth rate and its size. Cessation of bainite reaction is not quantified explicitly in this nucleation-based model. The diffusional approach considers only the growth rate of one single plate but not that of a subunit as a member of a bainite sheaf. Autocatalytic nucleation of subunits, which plays a significant role in formation of bainite sheaf and affects the overall kinetics of the bainite reaction, is not taken into account.
3.2 Literature Review

Common deficiencies associated with both approaches can be summarized as follows. Neither model can predict the width of subunits, which is the characteristic length in controlling the strength of bainitic structures. Strain energy accompanying the formation of bainitic ferrite governs the size, aspect ratio and dislocation density of subunits. A realistic model has to incorporate this factor as well. However, in the framework of diffusion model the kinetic role of the plastic accommodation in austenite was evaluated by Quidort and Bouaziz [103], which seems to be a phenomenological quantification. Substitutional elements seem to slow down the rate of bainitic ferrite formation by changing the thermodynamic boundary conditions, and by means of interaction with the moving \( \alpha/\gamma \) interface, i.e. by a solute drag effect. Transformation stasis, i.e. the so called “incomplete reaction phenomenon”, can also be related to this interaction. The solute drag effect has to be introduced rigorously into the kinetic model. The intrinsic mobility of the \( \alpha/\gamma \) interface, which is a measure of the rate of lattice change from FCC to BCC, can be rate controlling at higher undercooling or lower carbon content. Thus it is crucial to include the nature of the \( \alpha/\gamma \) interface and its mobility into the model. Current models are not capable of handling the morphology transition of ferrite from allotriomorphic ferrite to Widmanstätten and bainitic ferrite that takes place through decreasing the transformation temperature.

Alternatively, in most steels, the overall kinetics of bainite transformation can be described by an Avrami equation [74]. Umemoto [75], proposed a modified form of this equation to include the effect of prior austenite grain size on the kinetics of phase transformation, as presented in section 2.1.2.6. The reported values for \( n \) and \( m \) are different from those of ferrite and pearlite. Umemoto et al. [75], suggested 4 and 0.6 for \( n \) and \( m \), respectively, for bainite formation between 300 and 450°C in SUJ2 steel, Fe-0.99C-0.24Si-0.29Mn-1.34Cr.
Bhadeshia [109] also reported a range of 1.8-4 for $n$ and a value of 0.65 for $m$. These suggested values indicate that nucleation and growth take place simultaneously and support the autocatalysis nucleation nature of bainite [109].
3.3 Study of Isothermal Bainite Formation in Fe-0.6C-1.5Mn-1.5Si

The goal of this part is to experimentally characterize the kinetics and microstructural features of bainite evolution from single phase austenite in Fe-C-Mn-Si alloying system. The material selected for this study was a laboratory steel with a nominal composition of 0.6C-1.5Mn-1.5Si (wt%). The steel was supplied as 10mm hot-rolled plate with a predominantly pearlitic initial microstructure. The \(A_e\) temperature of the investigated steel was determined as 755°C using Thermo-Calc software with Fe2000 database.

The examined composition resembles the chemistry of the intercritically treated austenite in classical 0.2wt%C TRIP steel at the start of bainite reaction, where due to presence of 40 to 60 volume percent of ferrite, the remaining austenite is enriched with carbon to approximately 0.6wt%.

3.3.1 Experimental procedures

A Gleeble 3500 thermomechanical simulator equipped with a contact dilatometer was employed to perform austenitization and transformation experiments. To establish suitable austenitization conditions, resulting austenite grain sizes were first studied by heat treating rectangular samples of 3×6×15mm. The selected austenitizing procedures were to heat the samples at a rate of 5°C/s to two different temperatures, i.e. 800 and 1050°C and hold for 1min resulting in volumetric austenite grain sizes, \(d_r\), of 13 and 40μm, respectively. Subsequent transformation tests were carried out using tubular specimens of 7mm diameter with 1mm wall thickness. A type-K thermocouple was spot welded on the outer surface of the tubular sample, right at the middle, where the volume change during the imposed thermal...
3.3 Bainite Formation in Fe-0.6C-1.5Mn-1.5Si

Chapter 3

cycle was measured by the attached dilatometer. Due to the unique capability of the Gleeble 3500, temperature can be controlled within a couple of degrees of the target temperature along any complex heating-cooling pattern. After austenitization at 800 and 1050°C, respectively, the tubular specimens were cooled using He gas at a rate of approximately 80°C/s to selected bainite reaction temperatures, where the kinetics of isothermal bainite formation was quantified by dilatometry measurements. The isothermal temperatures applied were 300, 350, 400 and 450°C for samples with the smaller austenite grains, and 350, 375, 400 and 450°C for specimens having the larger prior austenite grains. In a second test series, the bainite formation was interrupted at the times for 10, 50 and 90 percent transformation and the samples were quenched to room temperature for microstructure characterization. It has to be noted that tests were performed using a vacuum of 1.3mPa (10⁻⁶ Torr) to prevent any potential oxidation or decarburization. The thermal path that the test specimens were subjected to is schematically depicted in Figure 3-5.

![Figure 3-5 Schematic representation of the heat treatment cycle applied to isothermally form bainite at different temperatures from a single phase austenite featuring 13 and 40μm volumetric grain size.](image)

Figure 3-5 Schematic representation of the heat treatment cycle applied to isothermally form bainite at different temperatures from a single phase austenite featuring 13 and 40μm volumetric grain size.
3.3 Bainite Formation in Fe-0.6C-1.5Mn-1.5Si

Surface preparation for metallography was accomplished by mechanical grinding of the mounted sample cut at the location of temperature and dilation measurements, followed by polishing using 0.05µm silicon solution as the final step. Then the specimens were etched in 2% nital solution to reveal the bainite microstructures, whereas the attacking time was varied to achieve the optimum contrast of the microstructural constituents. To reveal the prior austenite grain boundaries, the as-quenched samples after austenitization had been tempered at 550°C for 24 hours to enhance segregation of impurities on the boundaries, followed by quenching to room temperature and etching using a solution containing 50ml picric acid, 0.4g wetting agent and 0.3g copper chloride. The etchant had been warmed up to 60-70°C and the Cu layer deposited on the examined surface was removed afterward using 10% hydroxide ammonium solution. To determine the EQAD (equivalent area diameter) of austenite grains Jeffries method outlined in ASTM standard E112-96 was adopted. One can convert the EQAD to volumetric austenite grain size by multiplying with a factor of 1.2 [132].

3.3.2 Experimental results

The dilatometer responses recorded during the bainite formation stage are summarized in Figure 3-6(a) and (b) for both austenitization conditions. In all tests a significant incubation period is observed thereby confirming that the selected cooling rate from austenitizing to bainite temperatures was sufficient to prevent any bainite nucleation along the preceding cooling path. The data illustrated in Figure 3-6a for the specimens with the prior austenite grain size of 13µm, indicate that both the duration of the incubation time and the time to completion increase with decreasing reaction temperature. Moreover, the total volume expansion recorded at the end of transformation increases as temperature is lowered and is
the largest for the lowest temperature, i.e. 300°C. Similarly, as shown in Figure 3-6b, more bainite tends to form as the reaction temperature drops when the initial austenite grain size is 40µm. However, the temperature trend of the bainite reaction rate is quite different here with the highest rate being observed for the lowest temperature, i.e. 350°C, and little dependence on temperature for the higher transformation temperatures.

![Figure 3-6 Dilatometer responses recorded during isothermal bainite formation at different temperatures from austenite grain sizes of (a) 13µm and (b) 40µm.](image)

Using the lever law the isothermal dilation was translated into normalized fraction transformed, based on which the TTT diagrams of bainite formation from the two different austenite grain sizes can be constructed. This diagram is depicted in Figure 3-7. It is clearly seen that larger austenite grain sizes lead to a delay of the bainite reaction, as for example indicated by $t_{5\%}$ for the start of transformation. Moreover, it can be seen that the rate of bainite formation from 40µm austenite grains displays a minimum at approximately 375°C.
Figure 3-7 TTT diagram of bainite formation from two different austenite grain sizes in Fe-0.6C-1.5Mn-1.5Si.

Typical optical and SEM microstructures of isothermally formed bainite in the temperature range of 350 to 450°C are presented in Figure 3-8 and Figure 3-9, respectively, for the prior austenite grain size of 40μm. For those specimens the isothermal transformation was interrupted after formation of about 50% bainite, followed by quenching to room temperature.

The volume fraction of bainite at the end of each isothermal reaction were measured based on the optical micrographs. The maximum fraction $\theta_B$ of bainite formed in each condition is summarized in Table 3-3.

<table>
<thead>
<tr>
<th>Transformation temperature, °C</th>
<th>$d_p=13\mu m$</th>
<th>$d_p=40\mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0.61</td>
<td>0.64</td>
</tr>
<tr>
<td>400</td>
<td>0.65</td>
<td>0.76</td>
</tr>
<tr>
<td>350</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>300</td>
<td>0.84</td>
<td>0.85</td>
</tr>
<tr>
<td>450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>375</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3 Bainite Formation in Fe-0.6C-1.5Mn-1.5Si

Chapter 3

Figure 3-8 Optical micrographs showing bainite (dark gray phase) surrounded by martensite/austenite matrix formed at (a) 450, (b) 400 and (c) 350°C from $d_f=40\mu m$.

In the optical micrographs, Figure 3-8a to c, bainitic ferrite can be seen as dark constituent embedded in either a martensite or retained austenite matrix. The bainite phase consists of subunits in the form of discrete packets. The morphology of the subunits at the highest reaction temperature, i.e. 450°C, resembles that of degenerate ferrite. Here, individual ferrite
grains can be detected while lath and plate morphologies tend to emerge in samples reacted at 400 and 350°C, respectively. The width of subunits decreases with temperature and their length is limited by the prior austenite grain diameter or the available gap between units already formed. Although, the primary nucleation sites were revealed to be mainly austenite grain boundaries, some evidence of autocatalytic nucleation was also observed at higher magnification levels.

3.3.3 Modeling

Modeling the bainite reaction is a matter of controversy because different mechanisms, i.e. edgewise diffusional growth and displacive transformation have been proposed. Here, different kinetic models, including semi-empirical approaches are employed to evaluate their predictive capabilities in the present case. This in particular helps to explore the potential benefits and inefficiencies of each examined methodology.

3.3.3.1 Semi-empirical modeling approach

To develop a semi-empirical model, the traditional Johnson-Mehl-Avrami-Kolmogorov (JMAK) methodology can be adopted, i.e. [74]:

\[
f = 1 - \exp\left[-b(t - \tau)^n\right]
\]

where \( f \) is the normalized fraction transformed, \( t \) is the time at transformation temperature, \( \tau \) denotes the incubation time; \( b \) and \( n \) are rate parameters. The parameter \( n \) is usually assumed to be temperature independent and can be determined by representing the experimental data in a plot of \( \ln \ln (1/f) \) vs \( \ln t \). However, the obtained quantity for \( n \) is quite sensitive to the value assigned for the incubation time. This may be one of the reasons that a wide range of \( n \) values, i.e. from 1 to 4, are reported in the literature [78,109,117]. The parameter \( b \) is then
3.3 Bainite Formation in Fe-0.6C-1.5Mn-1.5Si

used to account for the effects of temperature and initial austenite grain size on the transformation kinetics such that [78]:

\[ b = \frac{b_0(T)}{d_r^m} \]  \hspace{1cm} (3-17)

where \( b_0 \) is a function of temperature and \( m \) is the grain size exponent.

Applying the JMAK approach to the present experimental kinetics of bainite formation, \( n=1 \) has been obtained employing the incubation times summarized in Figure 3-10. Then, \( b \) has been determined from a best fit analyses of the individual transformation curves. Figure 3-11 shows \( b \) as a function of temperature for both initial austenite grain sizes. A linear temperature dependency of \( \ln b \) has been proposed elsewhere for ferrite [21] and can here be applied for the transformations below 450°C for \( d_r = 13\mu m \) and above 350°C for \( d_r = 40\mu m \) such that:

\[ \ln b = -5.4d_r^{0.14} + 0.00487T \]  \hspace{1cm} (3-18)

where the temperature is in °C and \( d_r \) in μm. Assuming the above relationship for \( \ln b \), the predicted kinetics are observed to be in good agreement with experimental data for all transformation temperatures except for those at 450°C for \( d_r = 13\mu m \) and at 350°C for \( d_r = 40\mu m \). Figure 3-12 illustrates the quality of the JMAK fit for the bainite transformation at 300 and 400°C \( (d_r =13\mu m) \), and 375 and 450°C \( (d_r =13\mu m) \). However, as evident from Figure 3-11, a more complex temperature function would have to be considered for \( b \) in order to replicate the experimental kinetics for all conditions. It is obvious that more experimental data are required to establish a conclusive function for \( b \).
Figure 3-10 Incubation times of bainite formation as a function of temperature for different austenite grain sizes, i.e. 13 and 40 μm.

Figure 3-11 Temperature dependency of the parameter b to provide optimal description of experimental data using the JMAK equation with n=1.
3.3.3.2 Modeling the incubation period

Incubation period of a reaction can in general be related to the nucleation kinetics and basically is referred to the time for establishing the steady-state condition in nucleation. However, nucleation itself as an atomic event is more elusive and complex than subsequent growth. Particularly, the debated nature of bainite, i.e. diffusive or displacive, constitutes a major challenge such that any conclusive description of the nucleation stage is still lacking for the bainite reaction. Therefore, here a rather phenomenological treatment based on the classical nucleation theory is adopted as a first attempt to predict the incubation period of bainite formation.

Assuming that the time for removing an atom from a critical nucleus is essentially similar to that for adding an atom to a cluster of subcritical size, i.e. the time for formation of a nucleus,
Russell [133] treated grain boundary nucleation and developed an expression for the incubation time, i.e.:

\[ \tau \propto kT \frac{n^*}{\Delta G^* \beta^*} \quad (3-19) \]

where \( n^* \) is the number of atoms embedded inside the critical nucleus, \( \Delta G^* \) is the activation energy for the formation of this nucleus and \( \beta^* \) is the frequency factor of jumps toward or from the critical nucleus. This factor is defined in terms of effective diffusivity that relates to boundary or volume diffusion, and the number of atoms in contact with the critical nucleus, \( k^* \), such that:

\[ \beta^* = \frac{k^* D_{\text{eff}}}{a_L^2} \quad (3-20) \]

where \( a_L \) denotes the lattice parameter. Various types of grain boundary nuclei featuring different geometries and coherency characteristics were analyzed by Russell to quantify the aforementioned parameters used in Equation 3-19. As a consequence, the incubation period can in general be represent by the following simplified expression:

\[ \tau \propto \frac{T}{\Delta G^n D_{\text{eff}}} \quad (3-21) \]

where the energy term is the driving pressure for nucleation and its exponent \( n \) takes either the value of 2 or 3 depending on the coherency of the forming nucleus. As also indicated by Bhadeshia [134], the above equation can be rearranged in the following format:

\[ \ln \frac{\Delta G^n \tau}{T} = Q_D / RT + C_1 \quad (3-22) \]

in which \( Q_D \) denotes the activation energy for the relevant diffusion process and \( C_1 \) is a constant embedding all the pertinent constants such as geometrical factor, interfacial energy
between matrix and precipitate, the wetting angle effect and the pre-exponential factor of the diffusivity term. To include the effect of prior austenite grain size, $d_r$, this constant is modified here as:

$$C_1 = C_2 d_r^n$$

(3-23)

Using Equation 3-22, the experimental incubation time of isothermal bainite formation, as already presented in Figure 3-10, was tried to be replicated. Table 3-4 shows the adjustable parameters obtained from the optimal fit to the measured data. The model predictions employing these values are also illustrated in Figure 3-13. It is evident that the model can capture most of the data points adequately. However, the shortest incubation times, which are associated with bainite formation at 450 and 350°C from $d_r$ of 13 and 40μm, respectively, were noticeably overestimated. The inaccurate prediction of the bainite kinetics for these two conditions has already been mentioned in the previous section and suggests that more experimental measurements have to be carried out to verify and characterize the kinetics in those temperature regions.

By virtue of the presence of a coherent interface between bainitic ferrite and the parent austenite, the parameter $\sigma$ was assumed to be 2 and an attempt was then made to find the corresponding values for other parameters. As indicated in Table 3-4 the value for the activation energy reported is about half of that for carbon diffusion in bulk austenite. Therefore it is plausible to speculate that grain boundary diffusion of carbon governs the nucleation kinetics. It has to be noted that even during displacive nucleation of bainite the partitioning of carbon is allowed, which constitutes one common conjecture adopted by the two different schools of thought. However, since the above analysis is a crude treatment of nucleation, and different sets of values for those parameters can yield acceptable predictions
as well, one can hardly draw a definite fundamental conclusion out of these data and its application is then solely confined for modeling purposes.

**Table 3-4 Parameters used in Equation 3-22 to predict the incubation period.**

<table>
<thead>
<tr>
<th>$\omega$</th>
<th>$Q_D$, kJ/mol</th>
<th>$C_2$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>55</td>
<td>1.64</td>
<td>-0.3</td>
</tr>
</tbody>
</table>

*Figure 3-13 Model prediction (lines) and experimental incubation period (points) of isothermal bainite formation from two prior austenite grain sizes, 13 and 40\(\mu\)m, in 0.6wt\%C-1.5wt\%Mn-1.5wt\%Si steel.*

### 3.3.3.3 Diffusion model

The diffusion model adopted here is based on the Zener-Hillert equation for edgewise growth of a plate in form of a circular cylinder with a tip curvature of $\rho$, as described in detail in section 3.2.8 using Equation (3-12). This equation, in which the supersaturation term is corrected to account for the Gibbs-Thomson effect, indicates that the growth rate depends on
the tip curvature. Usually, for a given value of the austenite-ferrite interfacial energy, $\sigma_{ay}$, a plate adopts the tip curvature that corresponds to the maximum growth rate, $\nu_{\text{max}}$. To evaluate the maximum growth rate the derivative of Equation (3-12) with respect to $\rho$ has to be calculated for each transformation temperature. For this purpose a numerical methodology was developed here, the detail of which is going to be described in the following paragraph.

The carbon diffusivity in austenite was quantified adopting Ågren’s equation [43] in which for the carbon concentration the equilibrium value in austenite at the examined temperature was used.

The interfacial carbon concentration, $X_{\rho}^V$, which can be quantified in terms of radius of the tip curvature and the austenite-ferrite interfacial energy, $\sigma_{ay}$, varies from $X_0$ to $X_{eq}^V$, the equilibrium carbon content in austenite, when $\rho$ increases from the critical radius for ferrite nucleation to infinity. This variation can be quantified by including the Gibbs-Thomson effect, $\sigma_{ay} V_m / \rho$, in the Gibbs free energy of ferrite and finding the corresponding carbon content of austenite in equilibrium with such a ferrite particle. For this purpose a FORTRAN program was designed to retrieve the required thermodynamic data from Thermo-Calc, construct the Gibbs energy curves of ferrite and austenite under paraequilibrium assumption and finally determine $X_{\rho}^V$ for each growth temperature adopting the approach outlined above.

The resulting calculation is represented in Figure 3-14. In the present calculation the value of $\sigma_{ay}$ was assumed to be 0.2J/m$^2$ [135]. The start of each curve corresponds to $\rho_c$, the critical tip curvature at which the Gibbs-Thomson effect would be equal to the driving pressure for nucleation from the parent austenite of $X_o$ composition. Therefore all the available driving pressure would be exhausted by the surface effect and no growth could be expected.
Consequently as $\rho$ changes and so does $X^\gamma_p$, the ratio $X^\gamma_p / \rho$, based on which the growth rate is defined, experiences a maximum. In fact, the growth rate tends to be zero at the critical tip curvature, $\rho_c$, passes through a maximum and afterward asymptotically approaches zero. This growth feature of a ferrite plate is illustrated in Figure 3-15 for the analyzed reaction temperatures.

After finding an expression for $X^\gamma_p$ as a function of $\rho$ and $\sigma_{ay}$, the derivative of Equation (3-12) was solved numerically to determine the radius at which the growth rate becomes a maximum. It was found that $v_{\text{max}}^\theta$ is essentially a linear function of the austenite-ferrite interfacial energy. This is shown in Figure 3-16 for bainite growth at 400°C, when the interfacial energy varies from 0 to 1J/m$^2$. 

Figure 3-14 Interfacial carbon concentration of austenite in equilibrium with ferrite plate bearing a tip curvature of $\rho$ for different temperatures.
3.3 Bainite Formation in Fe-0.6C-1.5Mn-1.5Si

Figure 3-15 The variation of growth rate with the tip curvature of a ferrite plate for different reaction temperatures assuming the Zener-Hillert model.

Figure 3-16 Variation of the maximum growth rate of a bainite plate with ferrite-austenite interfacial energy, calculated for bainite formation at 400°C in 0.6wt%C-1.5wt%Mn-1.5wt%Si steel.

The isothermal fraction of bainite can then be calculated by means of the following equation for the transformation rate, i.e. [131,136]:

\[ v_{\text{max}} \]
\[ \frac{df_B}{dt} = K_D v_{\text{max}}^B (1 - f_B) \]  

where \( K_D \) is a temperature dependent parameter which is associated with nucleation but has to be determined from experimental data. As proposed by Suehiro et al. [136], an Arrhenius relationship is employed for \( K_D \) with:

\[ K_D (m^{-1}) = \frac{2.18 \times 10^{-6}}{d_\gamma^{1.2}} \exp \left[ \frac{2770}{T} \right] \]

being obtained in the present case. Assuming that the diffusional growth starts after the incubation period has elapsed, the quality of fitting experimental kinetics is similar to that obtained with the semi-empirical approach. Again, a more complex function for \( K_D \) would be required to achieve a satisfactory agreement at 450°C for \( d_\gamma = 13 \mu m \) and at 350°C for \( d_\gamma = 40 \mu m \), respectively. As an example, typical predictions of the diffusion model using the above \( K_D \) are shown in Figure 3-17.

![Figure 3-17](image.png)

*Figure 3-17 Comparison of the measured kinetics and the predictions of diffusion model for isothermal bainite formation in 0.6wt%C-1.5wt%Mn-1.5wt%Si steel.*
3.3 Bainite Formation in Fe-0.6C-1.5Mn-1.5Si

3.3.3.4 Kinetic effect of strain energy in diffusion model

The formation of bainitic ferrite is associated with both types of dilatational and shear stresses due to shape change. The former arises from the specific volume difference between austenite and ferrite and the latter yields to the so-called surface relief effect. The elastic strain energy of bainite formation is estimated to be about 400 J/mol and is considered as criterion for displacive growth as discussed in section 3.2.5. If the amount of stress at the interface exceeds the yield strength of austenite then some plastic accommodation is likely to occur. On this basis the kinetic effect of strain energy, in terms of energy dissipation due to plastic accommodation, has been implemented into the diffusion model and is adopted here to verify if the predictive capability of the diffusion model can be improved.

Assuming that the entire transformation shear is accommodated plastically in the untransformed austenite, Quidort and Bouaziz [103] estimated the amount of this plastic work as:

$$dG_{\text{plastk}} = T_r \gamma_B \frac{df_B}{1 - f_B} V_m$$  \hspace{1cm} (3-26)

where $T_r$ is the yield strength of austenite that deforms as an ideal plastic medium, $\gamma_B$ is the shear component of transformation strain considered to be 0.22, and $f_B$ denotes the fraction of bainite. The energy dissipation due to the plastic work increases as the reaction proceeds. As a consequence the effective driving pressure, $\Delta G_{\text{int}} - G_{\text{plast}}$, that remains to render the diffusional growth decreases correspondingly. This implies that the maximum growth rate of a bainite plate, i.e. $v_{\text{max}}^B$, is no longer constant at a given reaction temperature and it tends to drop as the transformation carries on. This is in contrast with the case that plastic
accommodation is neglected during the diffusional growth of a bainite plate, i.e. bainite plates grow featuring constant velocity.

To quantify the variation of $v_{\text{max}}^B$ with the fraction of bainite, first the dissipation of energy as a function of fraction was evaluated using Equation 3-26. The expression proposed by Bouaziz et al. [137] had been adopted to account for the temperature dependency of austenite yield strength, as given by ($T$ in °C):

$$
\tau_y^a(T) = \tau_y^a(20) \exp[-0.0011(T - 20)]
$$

For each bainite fraction, after removing $G_{\text{plastic}}$ from the chemical driving pressure, the maximum growth rate was determined following the methodology described in section 3.3.3.3. As an example, the variation of $v_{\text{max}}^B$ with bainite fraction for growth at 400°C is illustrated here in Figure 3-18. The dashed line shows the constant growth rate when no plastic accommodation is considered.

![Figure 3-18 Decreasing trend of the growth velocity of a plate as bainite fraction increases, transformation at 400°C in 0.6wt%C-1.5wt%Mn-1.5wt%Si steel.](image)

151
Accounting for the energy dissipation by plastic work simply results in slowing down the rate of bainite formation in particular as the reaction approaches to its completion. The fraction of bainite can then be calculated using the rate equation as given by Equation (3-24) and considering the fraction dependency of $v_{\text{max}}^b$ for each transformation temperature. From the optimum description of the experimental kinetics of bainite formation in 0.6wt%C-1.5wt%Mn-1.5wt%Si steel, the following temperature dependency was found for $K_D$, i.e.:

$$K_D (m^{-1}) = \frac{2.78 \times 10^{-6}}{d_{\gamma}^{1.15}} \exp \left[ \frac{3170}{T} \right]$$

(3-28)

A typical prediction of diffusion model modified by the effect of plastic accommodation is illustrated in Figure 3-19 for isothermal bainite evolution at different temperatures from $d_\gamma$ of 13 and 40 $\mu$m.

Figure 3-19 Prediction (lines) of diffusion model modified with the effect of plastic work and the experimental kinetics (points) of bainite formation in Fe-0.6wt%C-1.5wt%Mn-1.5wt%Si alloy.
3.3 Bainite Formation in Fe-0.6C-1.5Mn-1.5Si

As it is evident the overall agreement between model calculation and the measured kinetics is fairly good. However, for the examined alloy it appears that accounting for plastic work in the diffusion model does not lead to a substantial improvement in its predictive capability, in particular for the highest reaction rates corresponding to bainite formation at 450 and 350°C for \( d_r \) of 13 and 40 \( \mu m \), respectively. Moreover, compared with the case when plastic work is neglected, i.e. Figure 3-17, it appears that for the bainite fractions above 0.7 the experimental data is being somewhat underpredicted when plastic work is taken into account.

3.3.3.5 Displacive model

In the displacive theory of bainite formation growth does not contribute to the overall kinetics, i.e. the rate of reaction is assumed to be controlled solely by nucleation. Moreover, in contrast to a diffusional-type of nucleation, the nucleation rate is a linear function of driving pressure. As described in section 3.2.6 the rate equation for isothermal bainite formation with displacive manner can be formulated by Equation 3-10, which is used here to describe the isothermal bainite formation in Fe-0.6wt%C-1.5wt%Mn-1.5wt%Si.

The variation of driving pressure, \( \Delta G \), with temperature for the investigated steel was quantified by means of thermodynamic data provided by Thermo-Calc assuming paraequilibrium condition. From the Thermo-Calc results, a simplified expression can be given for the temperature range of 300 to 500°C, i.e.:

\[
\Delta G (J/mol) = 7.017 - 4653.5 
\]

when \( T \) is in °C.

As natural starting point, first the reported values for the three adjustable parameters, i.e. \( K_1 \), \( K_2 \) and \( \beta \) as depicted in Table 3-1, were employed to predict the bainite evolution kinetics. Using the two sets of fit parameters, no satisfactory description of the present results in the
3.3 Bainite Formation in Fe-0.6C-1.5Mn-1.5Si

0.6C-1.5Mn-1.5Si steel were obtained. Thus, the model parameters were adjusted to provide the best fit possible with the eight experimental curves. Given the limited database it was possible to use different fit procedures with similar fit quality. For example, setting $K_2$ to zero (i.e. eliminating the role of driving pressure) or assuming $\beta = 0$ yield quite similar results in terms of fit quality which cannot be improved by also varying this third parameter, i.e. $\beta$ and $K_2$, respectively. As an example, the parameter set with $\beta = 0$ obtained for the present 0.6C-1.5Mn-1.5Si steel is shown in Table 3-5. A typical comparison of model predictions with the measured kinetics for the bainite formation at various temperatures in specimens with $d_\gamma=40\mu m$ is illustrated in Figure 3-20.

<table>
<thead>
<tr>
<th>Values determined for 0.6C-1.5Mn-1.5Si steel</th>
<th>$K_1$, m$^3$s$^{-1}$</th>
<th>$K_2$, J/mol</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.6 \times 10^{-8} / d_\gamma$</td>
<td>553</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

*Figure 3-20 Displacive model predictions and the measured kinetics of bainite reaction for $d_\gamma=40\mu m$.  

Table 3-5 Values for adjustable parameters found for the 0.6C-1.5Mn-1.5Si steel in this work*
Reasonable agreement was found for all transformation conditions, except for those at 450°C for \( d_r = 13\mu m \) and at 350°C for \( d_r = 40\mu m \). These are the conditions were also the JMAK approach and the diffusion model in conjunction with simplified temperature functions for the parameters \( b \) and \( K_D \), respectively, failed to describe experimental results adequately.

### 3.3.4 Summary and remarks (0.6C TRIP steel)

Isothermal austenite-to-bainite transformation kinetics were analyzed for a Fe-0.6C-1.5Mn-1.5Si steel as a first step to develop a bainite transformation model for TRIP steels. Existing modeling approaches, i.e. the JMAK equation as well as a diffusional theory and the displacive model of Rees and Bhadeshia, have been evaluated. Using the general temperature trends of the respective model parameters, as proposed in the literature, the bainite formation can be equally well described with all three approaches. To further illustrate these findings, the calculations of displacive model and diffusion approach are summarized in Figure 3-21, in which a comparison between the predicted and the measured transformation time for 50% bainite formation, i.e. \( t_{50\%} \), are provided for all the examined transformation temperatures and austenite grain sizes. Clearly, the description of \( t_{50\%} \) is acceptable except for the specimens with the highest transformation rate for each austenitizing condition, i.e. at 450°C for \( d_r \) of 13\( \mu m \) and at 350°C for \( d_r \) of 40\( \mu m \), respectively.

For all the examined approaches significant deviations of predicted and observed kinetics have to be registered for the highest transformation rate at each austenitizing condition. Thus, additional careful experimental studies are required to develop new temperature dependencies of these model parameters. Further, it was shown that Russell’s treatment, which is consistent with the diffusional mechanism, can serve as the basis for developing a
submodel for the incubation time. This submodel appears to be a critical component of any model approach for bainite formation.

Figure 3-21 Comparison of the experimental data for the time of 50% transformed, $t_{50\%}$ and model predictions employing diffusion and displacive approaches.
3.4 Study of Isothermal Bainite Formation in Fe-0.18C-1.55Mn-1.7Si

In this part of research an attempt has been made to explore the kinetics and microstructural aspects of isothermal bainite formation after intercritical treatment, i.e. from a mixture of ferrite and austenite. Although bainite evolution in TRIP steels has received comprehensive experimental characterization [138,139], the major goal of the present study is to gain more insight pertinent to the critical aspects that are particularly significant for modeling purposes.

3.4.1 Experimental procedure and results

The examined material was a lab cast steel with a nominal composition of 0.18wt%C-1.55wt%Mn-1.7wt%Si, provided as hot forged blocks by Dofasco Inc. The as received microstructure consisting of ferrite + pearlite mixture was revealed to be extensively banded. Therefore, rods of 12mm diameter and 15cm length were machined, encapsulated in a quartz tube under rough vacuum and homogenized for 7 days at 1200°C. To remove the resulting coarse microstructure, this treatment was later followed by reheating the specimen to 980°C, holding for 2min and controlled cooling at rate of 1°C/s down to 450°C, which results in appropriate fine aggregates of ferrite + pearlite polygonal phases for the subsequent experiment.

In a similar manner as outlined earlier, a Gleeble 3500 thermo-mechanical simulator was employed to conduct a number of predetermined thermal cycles in this study. Tubular specimens were ramp heated to the austenitizing temperature, i.e. 980°C, held for 1min followed by cooling to the intercritical region where holding for 5min at 700°C yielded to a two phase microstructure consisting of 58% ferrite and 42% austenite. The samples were subsequently cooled at about 100°C/s to the bainitic temperature region, i.e. between 300 to
400°C, and held at predefined times to transform isothermally. The aforementioned thermal pattern is schematically represented in Figure 3-22.

![Figure 3-22 Thermal cycle designed to form bainite from intercritically treated specimens with 0.18wt%C-1.55wt%Mn-1.7wt%Si initial composition.](image)

The optical microstructures of specimens transformed partially to bainite at 400 and 300°C are illustrated in Figure 3-23. Here, the bainite reaction was interrupted after 50% progress by helium quenching to ambient temperature. The matrix consists of polygonal ferrite and the prior intercritical austenite has partially been transformed isothermally to bainite (dark gray phase) and potentially to martensite (light gray phase) upon quenching to room temperature. Well-defined bainite pockets consisting of many plates/laths are evident. At lower growth temperature the bainite tends to adopt lenticular plate morphology with smaller thickness whereas at higher temperature, i.e. 400°C bainite plates are coarser and represent the same thickness along their entire section. In both cases the growth of plates is impeded by the prior
3.4 Bainite Formation in Fe-0.18C-1.55Mn-1.7Si

austenite-ferrite boundaries, i.e. the length of the largest plate is the same as the austenite grain size.

![Optical micrographs of intercritically treated samples transformed partially to bainite at 400 and 300°C. Ferrite matrix (white) estimated to be 58%, and the rest is a mixture of martensite (light gray) and packets of bainite (dark gray), 2% nital etched.](image)

The characterization of microstructure by SEM technique, shown in Figure 3-24, confirms the previous information obtained from optical micrographs. However, it reveals many plates intersecting with each other and shows some indications of nucleation at pocket boundaries.
3.4 Bainite Formation in Fe-0.18C-1.55Mn-1.7Si

Figure 3-24 SEM micrographs of intercritically treated samples transformed partially to bainite at 400 and 300°C.

The dilation measurements recorded during isothermal holding at different temperatures are illustrated in Figure 3-25. The total volume change corresponding to the end of the reaction increases as growth temperature was lowered, indicating more bainite forms at higher undercoolings. Further the overall rate of reaction increases with decreasing temperature as well. It was found even after prolong holding, beyond the period that is shown in Figure
3-25, the dilation curves do not drop and follow a flat plateau. This rules out any significant precipitation of carbides that potentially might be expected at longer isothermal holding time and would be associated with an abrupt drop in dilation curve. It is also worth remarking that in spite of very fast cooling from intercritical to bainite region, about 100°C/s, no appreciable incubation period (less than a few seconds) was recorded. Therefore it is assumed that the incubation period is negligible and bainite transformation starts once the specimen reaches the target temperature.

![Kinetics of isothermal bainite evolution from intercritically treated samples featuring 42% austenite.](image)

Figure 3-25 Kinetics of isothermal bainite evolution from intercritically treated samples featuring 42% austenite.

To further investigate the transformation behavior of an intercritically treated austenite embedded in a ferrite matrix, a number of specimens were cooled down at different rates from 700°C to ambient temperature. Those samples had been processed in the two-phase field similar to the previous cases, i.e. reheating to 980°C and holding 5min at 700°C. By analyzing the dilatometry data measured along the cooling path, the start temperature of the transformation was determined for each cooling rate. It turned out that for a relatively large
range of cooling rates, i.e. from 24 to 155°C/s, the observed transformation start temperature remains rather constant around 275°C. This temperature is well below the bainite formation region examined in the previous experiments. Considering 58% ferrite with a nominal carbon content of about 0.02wt%, the carbon enrichment of the intercritical austenite is estimated to be about 0.41wt%C. Using Steven-Haynes [106] equation a martensite start temperature of about 295°C is then predicted for this intercritical austenite, which is in reasonable agreement with the experimental findings.

The determination of the critical cooling rate above which the pearlite/bainite formation can be suppressed is crucial for advanced high strength steels. In DP steels, the remaining austenite is expected to transform entirely to martensite. In TRIP steels having this information aids to design the appropriate thermal cycle parameters, i.e. the imposed cooling rate from intercritical region that prevents acicular/pearlite formation, and the temperature range of isothermal holding in the bainite region.

3.4.2 Modeling

The measured kinetics of isothermal bainite formation from a mixture of ferrite-42% austenite was analyzed using available modeling approaches, similar to the strategy adopted in section 3.3.3. For this purpose the dilation data represented in Figure 3-25 was first translated into normalized fraction. As starting point, the semi empirical methodology, i.e. JMAK equation as expressed by Equation (3-16), was employed. The optimal description of the experimental kinetics was accomplished by assuming \( n = 1 \) and considering the following temperature dependence for the \( b \) parameter:

\[
\ln b = -8.7 + 0.0097T
\]  

(3-30)
The predictions of the JMAK equation using these values for $n$ and $b$ are compared with the measured fraction in Figure 3-26. Apart from a slight overestimation of the fraction at final stages of the reaction at 400°C, the overall fit quality is satisfactory.

![Figure 3-26 Comparison of model prediction adopting JMAK approach and the experimental fraction of bainite formed after intercritical treatment in 0.18wt%C-1.55wt%Mn-1.7wt%Si steel.](image)

On the second attempt the kinetics of bainite evolution was simulated assuming diffusion-controlled edgewise growth of plates at constant rate as delineated in section 3.3.3.3. It has to be noted that the parent austenite, due to being treated in the intercritical region, has a carbon concentration of about 0.41wt%. Then assuming an interfacial energy between bainitic ferrite and austenite to be 0.2 J/m$^2$ the maximum growth rate for each transformation temperature was evaluated. Table 3-6 shows these growth velocities which were used to predict the isothermal kinetics of bainite formation by means of Equation (3-24). In the present analysis it was found that the experimental data can be accurately described, when $K_D$ is taken to be:

$$K_D (m^{-1}) = 18.5 \exp \left[ \frac{13000}{T} \right]$$

(3-31)
3.4 Bainite Formation in Fe-0.18C-1.55Mn-1.7Si

For comparison purpose the results of this simulation are presented in Figure 3-27 together with the measured kinetics of isothermal bainite formation.

Table 3-6 Growth rate of bainite plates for different transformation temperatures assessed using Zener-Hillert equation (0.41wt%C-1.55wt%Mn-1.7wt%Si austenite).

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>300</th>
<th>350</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_{\text{max}}^{p} ), ( \mu \text{m/s} )</td>
<td>9.9</td>
<td>22.2</td>
<td>39.5</td>
</tr>
</tbody>
</table>

Figure 3-27 Model prediction adopting diffusion approach and the experimental kinetics of isothermal bainite evolution from an intercritically treated austenite with carbon content of 0.41wt%.

Finally, employing the methodology as discussed in section 3.3.3.5, the displacive model was adopted to simulate the kinetics. By means of Thermo-Calc the driving pressure, \( \Delta G \), for ferrite nucleation from 0.41wt%C-1.55wt%Mn-1.7wt%Si austenite was quantified to be linear for the temperature range of 300 to 400°C, i.e.:
The main adjustable parameters in the displacive model, i.e. $K_1$, $K_2$ and $\beta$, were determined from the best fit to the experimental kinetics. Table 3-7 shows the model parameters for this case. The parameter dealing with autocatalytic nucleation, $\beta$, was found to be zero. Further, $K_2$ features the same order of magnitude as that reported by Bhadeshia [23] based on the extended data set (see Table 3-5). For the present analysis, $K_1$ appeared to be about two to three orders of magnitude larger than what was found before for bainite formation from single austenite phase in Fe-0.6wt%C-1.5wt%Mn-1.5wt%Si with $d_y$ of 13 and 40\,\mu m, respectively. This can be attributed to the faster rate of bainite formation from an austenite-ferrite aggregate where bainitic ferrite nucleates or perhaps continues to grow from austenite-ferrite interphase boundaries. The lack of incubation period prior to the onset of bainite growth, as shown in Figure 3-25, can also be related to this conjecture.

The predictions of the displacive model using the parameters reported in Table 3-7 are illustrated in Figure 3-28 along with the experimental fraction of bainite formation. The overall agreement between the calculation using the displacive approach and the measured data is, while still satisfactory, not as good as for example when the diffusion model is employed.

### Table 3-7 Parameters used in displacive approach to describe the measured kinetics of bainite formation from an intercritically treated austenite with carbon content of 0.41wt%.

<table>
<thead>
<tr>
<th>$K_1$, m$^3$s$^{-1}$</th>
<th>$K_2$, J/mol</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>$5\times10^3$</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 3-28 Comparison of the model prediction based on the displacive approach and the measured kinetic of isothermal bainite formation from an intercritically treated austenite with carbon content of 0.41wt%
3.5 Study of Continuous Cooling Bainite Formation in 0.19C-1.5Mn-1.6Si-0.2Mo TRIP Steel

In this section the kinetics of bainite formation during continuous cooling treatments is dealt with. This is relevant to the industrial processing of hot-rolled TRIP steel, where hot band is cooled slowly through the intercritical region to form the desired fraction of polygonal ferrite followed by coiling, such that the untransformed austenite decomposes partially into bainite. The material selected for this study was a Mo-TRIP steel containing 0.19wt%C-1.5wt%Mn-1.6wt%Si-0.2wt%Mo. The kinetics of austenite decomposition along different cooling paths had been measured earlier [140 ] by means of dilatometry using the Gleeble 3500 thermo-mechanical simulator. During the austenitization stage the test specimens were reheated at the rate of 5°C/s to different temperatures, i.e. 950, 1000 and 1100°C, held for 2min followed by cooling to deformation temperature 850°C, where the samples were subjected to a strain \( \varepsilon = 0, 0.3 \) and 0.6 at a strain rate of 1s\(^{-1}\). As a result the parent austenite has different features, in terms of the grain size, i.e. 24, 34 and 52μm, and the degree of work hardening. The list of experimental treatments that the examined material had been exposed to is shown in Table 3-8. The transformation start and finish temperatures of each product, i.e. ferrite and bainite are also included in the table. The true fraction of ferrite and bainite in the final microstructures, quantified using standard metallographic procedures, are outlined in the table as well. Based on the amount of ferrite formed preceding to bainite reaction, the degree of carbon enrichment in the untransformed austenite can be estimated as is indicated by \( c_{\gamma,\text{untrans}} \). Assuming a spherical austenite grain with an outer shell of ferrite, it is also possible to assess the grain diameter of the remaining austenite at the end of ferrite formation stage, which is listed by \( d_{\gamma,\text{untrans}} \) in the table. Therefore, both the carbon content and the size of the
starting austenite for bainite reaction might be different for each thermal path and have to be considered explicitly in the modeling analysis. The carbon enrichment in austenite is expected to be the more significant effect for the subsequent bainite formation.

Table 3-8 List of experimental treatments and the ensuing measurements of 0.16wt%C-1.5wt%Mn-1.6wt%Si-0.2wt%Mo, Mo-TRIP steel.

<table>
<thead>
<tr>
<th>Prior Austenite</th>
<th>Ferrite</th>
<th>Untransformed Austenite</th>
<th>Bainite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reheating</td>
<td>Strain, ε</td>
<td>CR, °C/s</td>
<td>T_s, °C</td>
</tr>
<tr>
<td>950°C, 24μm</td>
<td>0</td>
<td>1</td>
<td>755</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>5</td>
<td>725</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>7.5</td>
<td>676</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>10</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>5</td>
<td>754</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>10</td>
<td>746</td>
</tr>
<tr>
<td>1050°C, 34μm</td>
<td>0</td>
<td>1</td>
<td>740</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>2.5</td>
<td>690</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>5</td>
<td>740</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>1</td>
<td>776</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>5</td>
<td>752</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>10</td>
<td>720</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>1</td>
<td>787</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>10</td>
<td>772</td>
</tr>
<tr>
<td>1100°C, 12μm</td>
<td>0</td>
<td>1</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>5</td>
<td>720</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>10</td>
<td>662</td>
</tr>
</tbody>
</table>

A typical measurement of the overall decomposition kinetics of austenite, in terms of fraction transformed versus temperature, for the case where the initial austenite of 24 μm grain size (reheating at 950°C) was cooled constantly at the rate of 5°C/s to ambient temperature, is illustrated in Figure 3-29a. It can clearly be seen that the overall decomposition is sequential which is characterized by the two (or three when martensite forms) distinct sigmoidal sub-curves observed along the measured kinetics. This feature turned out to be common for most of the thermal treatments applied to the examined Mo-TRIP steel. Figure 3-29b shows the
3.5 Bainite Formation in Fe-0.19C-1.5Mn-1.6Si-0.2Mo

variation of the transformation rate with temperature evaluated based on the derivative of the data presented in Figure 3-29a. It is evident that for each transformation product a corresponding separate peak in the rate can be detected, which was also used to confirm the transformation start and finish temperatures of ferrite and bainite reactions.

![Graph A](image)

![Graph B](image)

Figure 3-29 Experimental data of overall austenite decomposition during continuous cooling treatments at 5°C/s after reheating at 950°C, ε=0 in 0.19wt%C-1.5wt%Mn-1.6wt%Si-0.2wt%Mo TRIP steel, (a) fraction transformed and (b) the rate of decomposition.
Considering the aforementioned data, in the following sections attempts will be made to model two major aspects of austenite to bainite transformation during continuous cooling paths, i.e. a criterion for the onset of bainite formation after ferrite reaction, and also the kinetics of bainite evolution in these circumstances.

3.5.1 Analyzing the onset of bainite reaction

As indicated in Figure 3-29b, at a certain point along the cooling path the rate of ferrite evolution appears to decline and shortly afterward further decomposition of the untransformed austenite is accomplished via bainite formation. This transition, i.e. the temperature at which bainite reaction comes into the picture, is of crucial significance in modeling the overall kinetics.

To analyze this transition point one could simply think of the relative growth rate of polygonal ferrite compared to that for a bainitic ferrite plate. Then naturally it is expected that bainite might form when it outgrows the polygonal ferrite, in terms of the growth velocity. The ratio of the two growth rates was quantified at the point of experimental transition for all the conditions reported in Table 3-8, however, no consistent trend was found to be followed. Alternatively, the driving pressure of bainitic ferrite formation at the experimentally observed transition point was calculated. For this purpose the carbon enrichment of the untransformed austenite was accounted for and paraequilibrium treatment was employed. The calculated driving pressure, as also outlined in the last column of Table 3-8, is plotted versus the transformation start temperature of bainite in Figure 3-30. It appears that regardless of the carbon content, grain size and degree of work hardening of the parent austenite, all the data points fall on the straight line showing a negligible scattering. This, at least as a first approximation, can constitute a phenomenological criterion for the onset of
bainite formation, i.e. along the cooling path following by ferrite evolution, bainite tends to emerge when a critical driving pressure is attained. For the examined Mo-TRIP steel this critical value is estimated as:

\[ G_{\text{Critical}} (J/mol) = 3.647T(°C) - 2240 \]  

(3-33)

Surprisingly, this linear dependence is of the same slope as the universal nucleation function \( G_N \) proposed by Bhadeshia (cf. section 3.2.5). However, the intercept given above, 2240J/mol, appears to be 300 J/mol larger than that indicated by \( G_N \). Although, the concept of the critical driving pressure, in terms of \( G_N \), was originally proposed as a criterion for displacive nucleation of bainite subunits, it is calculated by virtue of carbon partitioning during the nucleation event. In other words it is the maximum thermodynamic driving
3.5 Bainite Formation in Fe-0.19C-1.5Mn-1.6Si-0.2Mo

Chapter 3

pressure for nucleation of ferrite from the parent austenite in paraequilibrium condition. The composition of the critical ferrite nucleus corresponds to one that provides the maximum driving pressure. Regarding the displacive nucleation, it would be of more physical sense if the driving pressure is calculated assuming the same carbon content for bainitic ferrite and austenite. This implies a self-inconsistency of the displacive model in providing a conclusive description of the nucleation stage.

Therefore, since the driving pressure in Equation 3-33 is evaluated assuming carbon partitioning, then approaching a critical value for the driving pressure at the onset of bainite reaction, can potentially be considered as a criterion for diffusional formation of bainitic ferrite.

3.5.1.1 Modeling bainite formation

The experimental data points required for modeling the kinetics of bainite evolution in the Mo-TRIP steel were taken from the measured overall kinetics, such that between the transformation start and finish temperatures of the bainite stage the sub-curve was cut and then converted to normalized values using the maximum experimental fraction of bainite. As an example and with reference to the overall kinetics represented in Figure 3-29, the corresponding bainite stage, in terms of normalized fraction versus transformation temperature, is shown in Figure 3-31. In the right side of the plot, the second scale is also included to show the true fraction of bainite, which had been determined from dilatometry analysis and verified by metallographic measurements.

To analyze the measured kinetics of bainite the diffusion model as described in section 3.3.3.3, is adopted here. This is in part due to the fact that the criterion for bainite start, as expressed by Equation 3-33, assumes carbon partitioning to calculated the driving pressure.
Further, bainite forms in the examined Mo-TRIP steel at relatively high temperatures, i.e. mostly between 600 to 350°C, the temperature range within which bainite is expected to form by a diffusional mechanism [131].

![Figure 3-31 Normalized fraction of bainite formed during continuous cooling with CR=5°C/s for reheating at 950°C in Mo-TRIP steel.](image)

Regarding the bainite evolution from austenite of different carbon content during continuous cooling paths, the first step to model the kinetics is to quantify the maximum growth rate of a plate, \( v^R_{\text{max}} \), as a function of carbon concentration and temperatures. This allows accounting explicitly for the impact of gradual carbon enrichment of austenite on the growth kinetics, as the bainite reaction proceeds during a non-isothermal treatment. For the investigated temperature range and carbon concentrations, the evaluated \( v^R_{\text{max}} \), using the methodology as described in section 3.3.3.3, is illustrated in Figure 3-32. For the sake of simplicity relevant to the numerical implementation of \( v^R_{\text{max}} \), the following expression was fitted to the calculated values:

\[ v^R_{\text{max}} = \text{fit expression} \]
where, the parameters $A_1$ to $A_5$ were found to be:

<table>
<thead>
<tr>
<th>$A_1$, $\mu$m/s</th>
<th>$A_2$, °C</th>
<th>$A_3$, wt%C</th>
<th>$A_4$, °C</th>
<th>$A_5$, wt%C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$9.25 \times 10^3$</td>
<td>113.6</td>
<td>0.74</td>
<td>525.4</td>
<td>-1.9</td>
</tr>
</tbody>
</table>

Figure 3-32 Variation of the maximum growth rate of a bainite plate with temperature and carbon concentration for Mo-TRIP steel.

Having quantified the maximum growth rate of a plate, one can calculate the kinetics of bainite formation during non-isothermal conditions by integrating the rate equation [cf. Equation (3-24)] along a given cooling path. Typical model predictions for the case of reheating at 1050°C, corresponding to a prior austenite grain size of 34μm, are illustrated in Figure 3-33. For the purpose of comparison the corresponding measured data points are also included in each plot.
Figure 3-33 Diffusion model prediction and the experimental kinetics of bainite formation for reheating at 1050°C and various subsequent treatments in Mo-TRIP steel.
In these simulations the following temperature dependence were used for the parameter $K_D$, which was determined based on the optimum description of all the experimental kinetics (listed in Table 3-8), i.e.:

$$K_D(m^{-1}) = \frac{5\times10^{-6}}{d_y^{0.35}} \exp\left(\frac{12000}{T}\right)$$ (3-35)

To summarize the predictions of the diffusion model for bainite formation in Mo-TRIP steel regarding all the reheating conditions and the subsequent thermo-mechanical treatments, the calculated temperatures for 50% transformation are compared with the corresponding experimental values in Figure 3-34. Overall, it is seen that the diffusion model can reasonably capture most of the experimental kinetics. However, it is quite obvious that common to all reheating conditions, the measured data points for a cooling rate of 1°C/s are overpredicted. Although a realistic justification for this discrepancy cannot be provided, one might argue that it may be associated with the potential interaction between substitutional solute and the moving ferrite-austenite boundaries. Basically for the slow cooling rates, e.g. 1°C/s, the sample spends more time at higher temperatures, therefore the transformation interface can readily be loaded with solute atoms that essentially slow down the apparent growth rate. In particular, the examined material in addition to manganese has about 0.2wt% Mo, which is known to have a strong tendency for segregation to ferrite-austenite interfaces. Alternatively, the discrepancy between the model prediction and the experimental kinetics for slow cooling rates can be attributed to the pinning effect of carbide particles. In the investigated Mo-TRIP steel bainite starts to form at relatively high temperature, i.e. around 600°C, during continuous cooling treatment. This temperature is much higher than the one is traditionally practiced for isothermal bainite formation in TRIP steels, i.e. 300 to 450°C, during which the carbide formation is delayed due to the presence of Si or Al. However, the
rate of carbide formation is expected to accelerate as temperature increases by virtue of the required mass transportation of carbon (and solute) in the lattice. Further, the high thermodynamic affinity of molybdenum for carbon atoms decreases the retarding effect of silicon on carbide formation. Therefore, at sufficiently high temperatures where atoms are of high mobility and provided that sufficient time is available, i.e. low cooling rates, carbide formation is expected.

![Graph showing predicted and measured T50% temperatures](image)

Figure 3-34 Comparison of the predicted (using the diffusion model) temperature for 50% transformation and the measured value for all the experiments listed in Table 3-8.

### 3.5.1.2 Diffusion model with plastic work

In the aforementioned analyses of the role of Gibbs energy dissipation, which occurs due to the plastic accommodation of the transformation strain, was not be accounted for. Aiming at improving the quality of the model predictions, in particular for the slowest cooling rate, i.e. 1°C/s, the contribution of the plastic accommodation is implemented in the diffusion approach for bainite formation in the Mo-TRIP steel. As delineated in section 3.3.3.4, the
amount of the Gibbs energy dissipation, and its retarding effect on growth rate, scales with the fraction transformed. Therefore, it is essential to quantify the decline of $v_{\text{max}}^B$ as a function of bainite fraction for a given carbon concentration of parent austenite and transformation temperature. An example of this variation is shown in Figure 3-35, which indicates that the growth rate of a plate can potentially be reduced by about a factor of two when the bainite fraction changes from zero to 0.75.

![Figure 3-35](image)

*Figure 3-35 Variation of the maximum growth rate with transformation temperature for different values of bainite fraction, i.e. different values of Gibbs free dissipation due to plastic work.*

The effect of the plastic accommodation in the equation for maximum growth rate can be accounted for through modifying the parameters $A_i$ to $A_5$ as a function of bainite fraction, i.e. $A_i = \Phi(f_B)$, where $f_B$ is the true fraction of bainite with respect to the untransformed austenite remaining after the ferrite formation stage. Considering the modified diffusion model, the resulting predictions for the temperature for 50% transformation, $T_{50\%}$, compared with the measured values are illustrated in Figure 3-36. The parameter $K_D$ employed in the simulations is slightly different from the previous analysis, i.e.:
3.5 Bainite Formation in Fe-0.19C-1.5Mn-1.6Si-0.2Mo

\[ K_D (m^{-1}) = \frac{3.62 \times 10^{-3}}{d_{\gamma}^{0.16}} \exp\left(\frac{12000}{T}\right) \]  

(3-36)

Apparently, the model calculations agree reasonably well with most of the measured data, however, similar to the prediction of the diffusion model without accounting for the plastic work, the experimental kinetics for the slowest cooling rate, 1C/s, are still significantly overestimated. This implies that implementation of the plastic work into the diffusion model does not markedly improve its predictive capability for bainite formation in the Mo-TRIP steel, although from a conceptual prospect it adds more physical creditability to the diffusion model.

![Graph](image)

*Figure 3-36 Comparison of the predicted (using the diffusion model and accounting for the plastic work) temperature for 50% transformation and the measured value for all the experiments listed in Table 3-8.*
3.6 Summary and Remarks (Bainite Formation)

The significance of bainite formation in processing of TRIP steels in particular, and DP steels to a lesser extent, is twofold. Firstly, it constitutes the essential stage during which the untransformed austenite enriches with carbon such that austenite is retained to room temperature in TRIP steels. Secondly, it is of crucial importance to determine the critical cooling rate above which bainite formation can be prevented.

Therefore, to gain more insight regarding bainite transformation a series of isothermal and continuous cooling treatments in three different steels was carried out. The materials selected for isothermal bainite formation were a high carbon TRIP steel with nominal composition of 0.6wt%C-1.5wt%Mn-1.5wt%Si and a classical TRIP steel containing 0.18wt%C-1.55wt%Mn-1.7wt%Si. In the former bainite formation from single phase austenite was studied while for the latter an intercritical mixture of ferrite-0.42%austenite was chosen as the starting microstructure for isothermal bainite reaction. Relevant to continuous cooling treatments, a Mo-TRIP with 0.19wt%C-1.5wt%Mn-1.6wt%Si-0.2wt%Mo composition was considered, where ferrite reaction precedes the bainite formation. The ensuing results based on the modeling and analysis of the experimental data are discussed as follows:

- In the framework of Russell’s treatment based on classical nucleation theory, the incubation time associated with isothermal bainite formation in 0.6wt%C-1.5wt%Mn-1.5wt%Si steel was captured successfully for various temperatures and initial austenite grain sizes.

- The isothermal kinetics of bainite evolution in TRIP steels can be described rather accurately by the JMAK equation, the diffusion model and the displacive
formulation. Therefore, based on these analyses a conclusive model, outperforming the other approaches in terms of predictive capability, cannot be suggested.

- The version of displacive model analyzed here, as a purely nucleation approach to predict the overall kinetics, deals with the autocatalytic nucleation and sheaf formation in a simplified manner. Its recent modification [114] has yet to be verified.

- Analysis of austenite decomposition during a non-isothermal treatment in Mo-TRIP steel revealed that following the formation of polygonal ferrite, bainite transformation starts when a critical driving pressure is attained. This critical driving pressure varies linearly with bainite start temperature and is calculated assuming carbon partitioning in paraequilibrium condition. Hence it is regarded as a diffusional criterion.

- Regarding bainite evolution during continuous cooling treatments of a Mo-TRIP steel, the diffusion model can reasonably capture most of the experimental kinetics. However, for the slowest cooling rate, i.e. 1°C/s, the measured rates were significantly overestimated. This might be related to the potential kinetic effects of substitutional solutes, e.g. solute drag effect, which is not addressed rigorously in the model. The other potential reason for this discrepancy might be due to carbide formation and the resulting pinning effect, which slows down the growth rate of bainite plates. These aspects call for more improvement and modification of the model.

- For the investigated isothermal and continuous cooling cases, it turned out that accounting for the effect of the plastic work does not improve the overall predictive capability of the diffusion model.
Chapter 4 : Overall Conclusion

A thorough microstructure model to describe austenite decomposition into ferrite and bainite under industrial processing conditions was developed. This is in particular relevant to hot-rolled advanced high-strength steels such as DP and TRIP products. To explicitly address all the undergoing microstructural events, the model elegantly integrates a number of components, each developed on a solid physical ground, into a monolithic module which can easily be implemented into an industrial process model. Consequently, the employed model parameters have clear physical meaning. Therefore, the model application can potentially be extended to conditions that have not been considered in laboratory experiments, i.e. new steel grades. This constitutes a unique overall feature of the proposed model. Specifically to the ferrite and bainite components the following characteristics are outlined.

4.1 Findings and Achievements

- To replace the traditionally used JMAK methodology in process modeling, a physically-based approach in the framework of a mixed-mode model is proposed for polygonal ferrite formation. Assuming paraequilibrium the retarding effect of alloying elements is accounted for by using a modified Purdy-Brechet solute drag model. It was identified that accounting for the solute-interface interaction in the mixed-mode approach is essential to adequately describe experimental kinetics. Moreover, the apparent artifact of original Purdy-Brechet theory was corrected by accounting for the intrinsic asymmetry of the segregation profile inside the interface.

The proposed austenite-to-ferrite model proved that it is capable of accurately describing the ferrite formation kinetics for different isothermal and continuous
cooling situations. The physically well-defined model parameters, which are introduced to describe the interfacial properties of the ferrite-austenite interface, were determined for a number of examined cases. Further systematic experimental investigations would provide the basis to quantify these parameters as a function of steel chemistry. This would then also increasingly provide better guidelines for the acceptable combination of the employed parameters for each new steel which is being analyzed. In this sense, the model provides a versatile tool to predict the transformation kinetics for industrial processing conditions where laboratory simulations are limited.

- Relevant to TRIP steels, a comprehensive experimental characterization of bainite transformation kinetics for isothermal and continuous cooling treatments were carried out. In the sense of describing the overall isothermal kinetics, the predictive capabilities of the JMAK equation, the diffusional formulation and the displacive approach were revealed to be similar. Due to the nature of the model parameters, which are determined entirely from fitting to experimental data, all approaches were employed in a semi-empirical manner. Therefore, proposing a conclusive model for bainite reaction remains a challenge and requires more investigation. Further, it was revealed that the plastic accommodation of the transformation strain does not have a noticeable effect in improving the prediction quality of the diffusion model.

- Assuming diffusional transformation mechanism, a criterion based on a critical driving pressure is presented to predict the onset of bainite reaction along a given cooling path. Regarding isothermal bainite formation the incubation period can be predicted using Russell’s theory. Relevant to the maximum growth rate of a bainite
Overall Conclusion

plate in terms of the Zener-Hillert equation, a numerical treatment was developed to determine its carbon and temperature dependencies. For the various conditions of parent austenite, in terms of grain size and carbon content, the diffusion model could reasonably describe the kinetics of bainite evolution during continuous cooling treatments of a Mo-TRIP steel. The diffusion model was employed to bring more consistency into the overall model since both the isothermal incubation period and the criterion for the onset of bainite formation have been quantified in the framework of a diffusional transformation mechanism.

4.2 Future work

- To further improve the physical credit of the ferrite model, it is also intended to account for the potential deviation from paraequilibrium condition, which may also aid to remove the apparent temperature dependency of the binding energy. At higher transformation temperatures, the partitioning domain of substitutional atoms is likely well extended beyond the interface region and the degree of redistribution tends to be so pronounced that it cannot be described merely by a solute spike. Since during the industrial processing conditions paraequilibrium is expected to prevail, the aforementioned modification does not have a major significance for conventional process modeling and it is of more academic interest.

- Although, the diffusional approach was proven to be capable in capturing the major kinetic aspect of bainite formation, to translate the growth rate into the overall kinetics an empirical parameter, $K_D$, has to be introduced. This parameter provides a phenomenological description of the nucleation event. A more sophisticated treatment
Overall Conclusion

of nucleation is required. In particular, the evolution of bainite sheaves and autocatalytic (also called sympathetic) nucleation, which is an inherent feature of the bainite reaction, has to be considered appropriately. Moreover, the assumption of carbide-free bainite for bainite evolution in TRIP steels needs to be revisited. The potential effect of carbide formation, in terms of pinning the ferrite-austenite interface and removing some supersaturation from the untransformed austenite, has to be addressed in the diffusion model. Finally, a more rigorous approach, compared to the description of Quidort and Bouaziz, to quantify the elastic and plastic strain energy of bainite reaction is required.

- The recent version of the displacive model [114], which relies on the extended area pertinent to nucleation on grain boundaries, and its general applicability have to be evaluated for bainite formation in TRIP steels.
REFERENCES

1. International Iron and Steel Institute website: www.worldsteel.org


187
APPENDIX (1) Sub-Lattice Model

According to the concepts of the sub-lattice model [26], the description of the free energy of either the ferrite or austenite phase for a ternary steel, e.g. Fe-Mn-C, is presented below. All the definitions presented below are consistent with the sub-lattice approach.

The above system is defined in terms of four compounds such that each pair of them occupies one sub-lattice, i.e. substitutional sub-lattice which contains Fe and Mn, and interstitial sub-lattice which is filled by C and interstitial vacancy. The ratio between the numbers of atomic site on the substitutional lattice to interstitial one is called site ratio, \( \eta \). This ratio is 1 for austenite and 3 for ferrite phase. The four components are defined by: \( Fe:C \), \( Fe:Va \), \( Mn:C \) and \( Mn:Va \), by which the composition of the system can be represented on a square, instead of the well known Gibbs triangle for a ternary system. However, since the composition of this system can be varied by only two ways, i.e. changing carbon (or vacancy) content in interstitial lattice and manganese (or iron) content in the substitutional lattice, then this four components aggregate resembles a ternary solution phase.

The square of composition is shown below:

![Composition Square](image)

To represent the concentration, the site fraction of each component is defined as:
\[ Y_i = \frac{X_i}{1-X_c} \text{ for } i=\text{Fe and Mn} \quad (A-1) \]

\[ Y_c = \eta \frac{X_c}{1-X_c} \quad (A-2) \]

The Gibbs free energy of either ferrite or austenite \((j=\alpha \text{ or } \gamma)\) can be represented by the contribution of different terms, standard free energy of unmixed components, entropy of mixing for an ideal solution, the excess energy due to non-ideality and the magnetic effect, i.e.:

\[ G^j = \circ G^j - TS^j_{\text{ideal}} + G^j_{\text{excess}} + G^j_{\text{magnetic}} \quad (A-3) \]

These contributions are quantified as:

\[ \circ G^j = Y_{Fe} Y_C \circ G^j_{FeC} + Y_{Fe} Y_{Va} \circ G^j_{FeVa} + Y_{Mn} Y_C \circ G^j_{MnC} + Y_{Mn} Y_{Va} \circ G^j_{MnVa} \quad (A-4) \]

\[ -TS^j_{\text{ideal}} = RT(Y_{Fe} \ln Y_{Fe} + Y_{Mn} \ln Y_{Mn}) + RT\eta(Y_C \ln Y_C + Y_{Va} \ln Y_{Va}) \quad (A-5) \]

\[ G^j_{\text{excess}} = Y_{Fe} Y_{Mn} Y_C L^j_{Fe,MnC} + Y_{Fe} Y_{Mn} Y_{Va} L^j_{Fe,MnVa} + Y_{Fe} Y_C Y_{Va} L^j_{Fe,C,Va} + Y_{Mn} Y_C Y_{Va} L^j_{MnC,Va} \quad (A-6) \]

where the standard Gibbs energy term for each component, \(\circ G^j\), and the interaction term between two components, \(L^j_{i,k}\), are normally defined in terms of the following temperature dependency:

\[ \circ G^j_i \text{ or } L^j_{i,k} = A + BT + CT \ln T + DT^2 + ET^3 + \frac{F}{T} + \frac{G}{T^2} + \frac{H}{T^3} \quad (A-7) \]

and \(A\) through \(H\) denote the SGTE (Scientific Group Thermodata Europe) parameters, which are quantified and reported for different alloying systems in the literature. It has to be noted that to obtain the molar Gibbs free energy, the aforementioned three contributions have to be multiplied by \((1-X_c)\).

The magnetic contribution to Gibbs free energy is usually considered for ferrite and can be estimated using the following expression [29]:

191
\[ G_{\text{magnetic}} = RTg(\tau_m)\ln(\beta_m + 1) \quad \text{(A-8)} \]
and \[ \tau_m = T/T_C \quad \text{(A-9)} \]

where \( \beta_m \) represents the magnetic momentum and for different temperature ranges, i.e. above and below the Curie temperature, \( T_C \), the function \( g(T/T_C) \) is given by:

For \( T>T_C \):

\[ g = 1 - \frac{1}{1.56} \left[ \frac{1.25}{\tau_m} + \left( \frac{711}{497} \right) \left( \frac{\tau_m^3 + \tau_m^9 + \tau_m^{15}}{6 + 135 + 600} \right) \right] \quad \text{(A-10)} \]

and for \( T<T_C \):

\[ g = -\frac{1}{1.56} \left( \frac{\tau_m^{-5} + \tau_m^{-15} + \tau_m^{-25}}{10 + 315 + 1500} \right) \quad \text{(A-11)} \]

It has to be noted that both \( T_C \) and \( \beta \) depend on the alloy composition, i.e.:

\[ T_C = Y_{Fe}Y_C T_1 + Y_{Fe}Y_{Va} T_2 + Y_{Mn}Y_C T_3 + Y_{Mn}Y_{Va} T_4 + Y_{Fe}Y_{Mn} Y_{Va} T_5 \quad \text{(A-12)} \]
\[ \beta_m = Y_{Fe}Y_C \beta_1 + Y_{Fe}Y_{Va} \beta_2 + Y_{Mn}Y_C \beta_3 + Y_{Mn}Y_{Va} \beta_4 \quad \text{(A-13)} \]

where \( T_i \) and \( \beta_i \) are parameters.
APPENDIX (II) Code for Paraequilibrium Calculation

FORTRAN subroutine to determine the paraequilibrium carbon contents of ferrite and austenite at a given temperature for a quaternary Fe-C-Mn-Si steel.

Definition of the variables and parameters:

**IWSG ( )**: Integer array for storage of data inside TQ workspace.

**I_fcc, I_bcc**: Index for fcc and bcc phase.

**I_Fe, I_Mn, I_Si, I_C**: Index for the constituents of alloy.

**Gm_fcc(), Gm_bcc()**: Array containing C mole fraction and Gibbs free energy of phases.

**SGM( )**: Array containing C mole fraction, Gibbs energy and its derivative for fcc and bcc after fitting to SPLINE function.

**NN**: Number of total moles in the system.

**T**: Temperature in K.

**P**: Pressure in Pa.

**X_alpha, X_gamma**: Equilibrium mole fraction of C in ferrite and austenite (input parameters).

**XP_alpha, XP_gamma**: Paraequilibrium mole fraction of C in ferrite and austenite (output parameters).

**Tmn, Tsi**: The ratio of mole fraction of Mn (and Si) to iron in the parent austenite (input parameters).

**XXC, XXMN, XXSI**: Mole fractions of C, Mn and Si along component ray of carbon.

**Kf, Kb**: Pointer.

**Jf, Jb**: Pointer.

```fortran
subroutine peq(T,x_alpha,x_gamma,Tmn,Tsi,xp_alpha,xp_gamma)
  implicit doubleprecision (a-h,o-z)
  common /tc/iwsg,i_fcc,i_bcc,ic,imn,isi,ife
  dimension iwsg(80000),gm_bcc(500,2),gm_fcc(500,2),sgm(3500,7),
  dimension xx(500),yy(500),yy2(500)
  doubleprecision nn
  p=101325.d0
  NN=1
  call tqsetc('P',-1,-1,P,num,iwsg)
  call tqsetc('N',-1,-1,NN,num,iwsg)
  call tqsetc('T',-1,-1,T,num,iwsg)
  kb=0
  call tqcsp(i_fcc,'SUSPENDED',iwsg)
  call tqcsp(i_bcc,'ENTERED',iwsg)
  do XXc=0,3*X_alpha,X_alpha/100.
    kb=kb+1
    XXmn=(1-XXc)*Tmn/(1+Tmn+tsi)
    call...
  enddo
end subroutine peq
```
\[ X_{Si} = (1 - XX_c) \times T_{Si} / (1 + T_{mn} + T_{Si}) \]

\[
\text{call \ tqsetc('X',-1,ic,XXc,num,iwsg)} \\
\text{call \ tqsetc('X',-1,imn,XXmn,num,iwsg)} \\
\text{call \ tqsetc('X',-1,isi,XXsi,num,iwsg)} \\
\text{call \ tqce(' ',0,0,0.0D0,iwsg)} \\
\text{call \ tqget1('GM',i_bcc,-1,gm\_dummy,iwsg)} \\
\]

\[ \text{gm\_bcc(kb,2)} = \text{gm\_dummy} \]
\[ \text{gm\_bcc(kb,1)} = xx_c \]

Enddo

\[ kf = 0 \]
\[ \text{call \ tqcsp(i\_fcc,'ENTERED',iwsg)} \\
\text{call \ tqcsp(i\_bcc,'SUSPENDED',iwsg)} \]

\[
do \ XXc=0,1.5*\_gamma,\_gamma/200. \]

\[ kf=kf+1 \]
\[ XXmn = (1 - XXc) \times T_{mn} / (1 + T_{mn} + T_{si}) \]
\[ XXsi = (1 - XXc) \times T_{si} / (1 + T_{mn} + T_{si}) \]

\[
\text{call \ tqsetc('X',-1,ic,XXc,num,iwsg)} \\
\text{call \ tqsetc('X',-1,imn,XXmn,num,iwsg)} \\
\text{call \ tqsetc('X',-1,isi,XXsi,num,iwsg)} \\
\text{call \ tqce(' ',0,0,0.0D0,iwsg)} \\
\text{call \ tqget1('GM',i\_fcc,-1,gm\_dummy,iwsg)} \\
\]

\[ \text{gm\_fcc(kf,2)} = \text{gm\_dummy} \]
\[ \text{gm\_fcc(kf,1)} = xx_c \]

Enddo

!----------------- Fitting the BCC data to a spline function----------------- !--------------------------for SPLINE see: Numerical recipe in FORTRAN-----------------

\[ n = \text{kb} \]

\[
do \ i=1,n \]

\[ xx(i) = \text{gm\_bcc(i,1)} \]
\[ yy(i) = \text{gm\_bcc(i,2)} \]

Enddo

\[ yp1 = (yy(2) - yy(1)) / (xx(2) - xx(1)) \]
\[ ypn = (yy(n) - yy(n-1)) / (xx(n) - xx(n-1)) \]

\[
\text{call \ spline(xx,yy,n,yp1,ypn,yy2)} \\
\]

\[ jb = 0 \]

194
do x=xx(1),xx(n),(xx(n)-xx(1))/10./n
    jb=jb+1
    call splint(xx,yy,yy2,n,x,y,yla)
    sgm(jb,1)=x
    sgm(jb,2)=y
    sgm(jb,3)=yla
endo
!
---------------- Fitting the FCC data to a spline function----------------------------------
!
n=kf
!
do i=1,n
    xx(i)=gm_fcc(i,1)
    yy(i)=gm_fcc(i,2)
endo
!
ypl=(yy(2)-yy(1))/(xx(2)-xx(1))
ypn=(yy(n)-yy(n-1))/(xx(n)-xx(n-1))
!
call spline(xx,yy,n,ypl,ypn,yy2)
!
jf=0
!
do x=xx(1),xx(n),(xx(n)-xx(1))/10./n
    jf=jf+1
    call splint(xx,yy,yy2,n,x,y,yla)
    sgm(jf,4)=x
    sgm(jf,5)=y
    sgm(jf,6)=yla
endo
!
!Finding ferrite and austenite carbon contents in paraequilibrium---
!---------------------------using common tangent line method-----------------------------
!
check=0
!
do i=1,jb
    do j=1,jf
        dt1=sgm(i,3)-sgm(j,6)
        dt2=sgm(j,5)-sgm(i,2)-sgm(i,3)*(sgm(j,4)-sgm(i,1))
        if(dt1.lt.1d-5.and.dt2.lt.1d-5)then
            Xp_alpha=sgm(i,1)
            Xp_gamma=sgm(j,4)
        endif
    enddo
endo
check=1.
exit
endif
enddo
if(check.eq.1)exit
enddo
return
end
APPENDIX (III) Code for NP-LE Calculation

FORTRAN subroutine to determine the NPLE carbon contents of ferrite and austenite at a given temperature for a quaternary Fe-C-Mn-Si steel.

```fortran
subroutine nple(t,xc,xmn,xsi,xn_alpha,xn_gamma,xn)
  implicit doubleprecision (a-h,o-z)
  common /tc/iwsg,i_fcc,i_bcc,ic,imn,isi,ife
  dimension iwsg(80000),xn(3,3)
  doubleprecision NN
  PP=101325.d0
  NN=1.d0
  call tgcsp(i_fcc,'ENTERED',iwsg)
  call tqcsp(i_bcc,'ENTERED',iwsg)
  do i=1,6
    call tqremc(i,iwsg)
  enddo
  call tqsetc('P',-1,-1,PP,num,iwsg)
  call tqsetc('N',-1,-1,NN,num,iwsg)
  call tqsetc('T',-1,-1,t,num,iwsg)
  call tqsetc('X1',-1,ic,Xc,num4,iwsg)
  call tqsetc('X',i_bcc,imn,Xmn,num5,iwsg)
  call tqsetc('X',i_bcc,isi,Xsi,num6,iwsg)
  call tqce(' ',0,0,0.0D0,iwsg)
  call tqgetl('ac',-1,ic,AC_C,iwsg) !XN( !bcc !NPL !fcc !)
  call tqgetl('X',i_bcc,ic,xn_alpha,iwsg)
  call tqgetl('X',i_bcc,imn,xn(2,1),iwsg)
  call tqgetl('X',i_bcc,isi,xn(3,1),iwsg)
  call tqgetl('X',i_fcc,ic,xn(1,3),iwsg)
  call tqgetl('X',i_fcc,imn,xn(2,3),iwsg)
  call tqgetl('X',i_fcc,isi,xn(3,3),iwsg)
  xn(1,1)=xn_alpha
  call tgcsp(i_fcc,'ENTERED',iwsg)
  call tqcsp(i_bcc,'SUSPENDED',iwsg)
  call tqsetc('ac',-1,ic,AC_C,num7,iwsg)
  call tqsetc('X',-1,imn,Xmn,num,iwsg)
  call tqsetc('X',-1,isi,Xsi,num,iwsg)
  call tqremc(num4,iwsg)
  call tqremc(num5,iwsg)
  call tqremc(num6,iwsg)
  call tqce(' ',0,0,0.0D0,iwsg)
  call tqgetl('X',-1,ic,xn(l,2),iwsg)
  call tqgetl('X',i_fcc,imn,xn(2,2),iwsg)
```

197
call tqget1('X',i_fcc,isi,xn(3,2),iwsg)  ! X ! !
call tqremc(num7,iwsg)

XN_gamma=xn(1,2)

return
end
APPENDIX (IV) Discrete Form of Fick’s Equations

The discrete form of the Fick’s equations for a moving boundary configuration is outlined in this Appendix. Considering the node configuration depicted below for both planar and spherical geometries, the node size is given by:

\[
\Delta z = \frac{\ell_o - \ell}{n - 1}
\]  

(A-14)

Then the following differential equation is employed to calculate the carbon profile in the remaining austenite: ($\kappa$ is 0 for planar and 2 for spherical geometry)

\[
\frac{c_i^{j+1} - c_i^j}{\Delta t} = \frac{c_{i+1}^j - c_{i-1}^j}{2\Delta z} \nu_i + \kappa \frac{D_i}{z_i} \frac{c_{i+1}^j - c_{i-1}^j}{2\Delta z} + \frac{D_{i+1}^j - D_{i-1}^j}{2\Delta z} \frac{c_{i+1}^j - c_{i-1}^j}{2\Delta z}
\]

\[
+ D_i \frac{c_{i+1}^j - 2c_i^j + c_{i-1}^j}{\Delta z^2}
\]  

(A-15)

The equation in the discrete form can be expressed as:

\[
\frac{c_i^{j+1} - c_i^j}{\Delta t} = \frac{(c_{i+1}^j - c_{i-1}^j)(n-i)}{2(\ell_o - \ell)} \frac{d\ell}{dt}
\]

\[
+ \kappa \frac{D_i(c_{i+1}^j - c_{i-1}^j)(n-1)^2}{2(n-i)(\ell_o - \ell)^2}
\]

\[
+ \frac{(D_{i+1}^j - D_{i-1}^j)(c_{i+1}^j - c_{i-1}^j)(n-1)^2}{4(\ell_o - \ell)^2}
\]

\[
+ D_i \frac{(c_{i+1}^j - 2c_i^j + c_{i-1}^j)(n-1)^2}{(\ell_o - \ell)^2}
\]  

(A-16)

where:
\[
\frac{d\ell}{dt} = \frac{D_1 (-3c_1^j + 4c_2^j - c_3^j)(n - 1)}{c_{eq} - c_{eq}^\alpha} \frac{2(\ell_o - \ell)}{2(\ell_o - \ell)}
\]
APPENDIX (V) Average Carbon Content of a Spherical Austenite

The numerical approach to calculate the average carbon content of the remaining austenite is depicted here. To fulfill the carbon mass balance in the system, the following equation has to be verified at each time step:

\[ c_0 = (1 - f_r)c^A + f_r c^r \]  \hspace{1cm} (A-17)

In case of carbon leakage or built up, then the fraction of the remaining austenite, containing the average carbon concentration of \( c^r \), must be corrected via changing the location of the interface. Therefore, at each time step the assessment of \( c^r \) for a given carbon profile is crucial. For spherical geometry, a linear carbon profile between two adjacent nodes is first assumed:

\[ c_i^r = c_i - \frac{c_i - c_{i+1}}{z_i - z_{i+1}} (z - z_i) \]  \hspace{1cm} (A-18)

the carbon content, \( Q_i \), of the austenite shell encompassed by these two nodes is given by:

\[ Q_i = \int_{z_i}^{z_{i+1}} 4\pi z^2 c_i^r dz = \int_{z_i}^{z_{i+1}} 4\pi z^2 (\Gamma z + \Lambda) dz \]  \hspace{1cm} (A-19)

\[ \Gamma = \frac{c_i - c_{i+1}}{z_i - z_{i+1}} \quad \text{and} \quad \Lambda = c_i - \frac{c_i - c_{i+1}}{z_i - z_{i+1}} z_i \]  \hspace{1cm} (A-20)

The average carbon of austenite then is the sum of \( Q_i \) over the volume of austenite sphere, \( V^r \):

\[ \bar{c}^r = \frac{1}{V^r} \sum_{i=1}^{n-1} Q_i \]  \hspace{1cm} (A-21)

which in the discrete format can be presented by this rather short solution, which is independent to the size of the remaining austenite and node size \( \Delta z \):
\[
\bar{c}^\gamma = \frac{0.25}{(n-1)^3} \sum_{i=1}^{n-1} \left[ (c_{i+1} - c_i)(n-i)(n-i-1)(2n-2i-1) + (3c_i + c_{i+1})(n-i)^3 - (c_i + 3c_{i+1})(n-i-1)^3 \right]
\]