Physically-based Modelling

of

Material Response to Welding
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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
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<tbody>
<tr>
<td>( A )</td>
<td>area</td>
<td>( m^2 )</td>
</tr>
<tr>
<td>( d )</td>
<td>atomic distance</td>
<td>( m )</td>
</tr>
<tr>
<td>( F )</td>
<td>specific thermodynamic driving force</td>
<td>( J m^{-3} )</td>
</tr>
<tr>
<td>( \mathcal{F} )</td>
<td>free energy of a system</td>
<td>( J )</td>
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<tr>
<td>( G )</td>
<td>Gibbs free energy</td>
<td>( J )</td>
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<tr>
<td>( \mathcal{H} )</td>
<td>enthalpy</td>
<td>( J )</td>
</tr>
<tr>
<td>( I )</td>
<td>welding current</td>
<td>( A )</td>
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<tr>
<td>( K )</td>
<td>JMAK material parameter</td>
<td>( s^{-1} )</td>
</tr>
<tr>
<td>( K^G )</td>
<td>grain growth material constant</td>
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<tr>
<td>( M_{ij} )</td>
<td>interface mobility between phases ( i ) and ( j )</td>
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<tr>
<td>( n )</td>
<td>JMAK growth mode exponent</td>
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<td>( \omega )</td>
<td>grain growth exponent</td>
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<td>potential nucleation sites of type-( j )</td>
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<td>( j )</td>
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<td>welding power</td>
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<tr>
<td>( v )</td>
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<tr>
<td>( \sigma )</td>
<td>specific interfacial energy</td>
<td>( J m^{-2} )</td>
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## Physical Constants

<table>
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<th>Units</th>
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<tr>
<td>( h )</td>
<td>Planck’s constant</td>
<td>( 6.63 \cdot 10^{-34} \ J \ s )</td>
</tr>
<tr>
<td>( k )</td>
<td>Boltzmann’s constant</td>
<td>( 1.38 \cdot 10^{-23} \ J \ (\text{atom} \ K)^{-1} )</td>
</tr>
<tr>
<td>( R )</td>
<td>Universal Gas Constant</td>
<td>( 8.31 \ J \ (\text{mol} \ K)^{-1} ).</td>
</tr>
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</table>
Note: The above list includes the frequently used symbols and constants in this thesis. In this document, subscript roman letters that are italicised will represent indices. Greek and non-italicised roman letters will serve as descriptors. Although care will be taken to maintain consistency, some situations demand the use of an already designated letter or symbol. In these cases, appropriate clarification will be given.
Part 1

Introduction and Review
Chapter 1

Introduction

1.1 General Introduction

The industrial importance of metal alloys, and in particular steels, has been growing and continues to grow. Next to availability, the reason for this industrial importance lies in the advances in materials science. Materials scientists continue to develop new alloys and methods of production, exploiting the manipulable properties of the metals to lead to improved performance for intended applications. These advances have demonstrated how important an alloy’s microstructure is for in-service performance. With the aid of tighter control over production conditions, manufacturers are able to deliver alloys with specific microstructures which are optimised for a specific application.

1.2 Influence of Welding

Production of the optimised base material for a given application or construction is an important step in delivering a product to the end-user, but it is not the final step. Nearly all material must undergo forming and joining processes after leaving the producer of the metal alloy. Forming has an influence on the final material properties, but the most important joining process, welding, has the strongest influence of all post-production treatments. In a weld, the carefully designed microstructure is destroyed and returned to an as-cast state. The microstructure next to the molten weld pool also experiences significant alterations, accompanied by the consequent degradation of material properties. In the fusion zone, the final alloy can be tailored by the addition of filler materials during welding, but the heat affected zone (HAZ) next to the weld cannot be readily improved during the welding process. This can, for example, result in significant weakening of the material next to the weld, unacceptable deformations to the welded product, or a combination of both.
1.3 Steels

Steels represent the most common metal alloy in industrial use today. The mechanical properties of these iron-based alloys can be manipulated by altering the composition, by the application of thermal treatments, by mechanical deformation, or a combination of these. Pure iron can exist in two solid state phases, which are characterised by the spatial configuration of the atoms. The smallest repetitive building block which uniquely describes this atomic configuration is called a unit cell. At room temperature, iron is stable as the ferrite phase, which has a body centred cubic (bcc) configuration with atoms at each corner of the cubic unit cell and one centred in the middle. At 910°C (1183 K), iron transforms into the austenite phase and the atoms are reorganised into the face centred cubic (fcc) configuration. The fcc configuration also has atoms at the corner of each unit cell, but also centred in each of the 6 faces of the cube. Upon further heating to 1390°C (1663 K), iron transforms back to the bcc configuration, but the high temperature bcc phase is termed delta-ferrite. Iron melts at 1534°C (1807 K). Addition of certain alloying elements can drastically alter these transition temperatures and can introduce new stable (or meta-stable) configurations of the atoms. The change in transformation temperatures and the presence of these phases can have a significant impact on how a steel responds to the welding thermal cycle, as well as on its retained mechanical properties. This makes steel a highly manipulable material, but also one for which it is difficult to develop general material models which capture effects of compositional variation and arbitrary thermal cycles.

1.4 Modelling

The purpose of material modelling can be seen as two-fold. The first goal is the furthering of knowledge concerning how and why an experimentally observed phenomenon occurs. A second objective is to use the knowledge gained from the first goal and apply it to the development of models which can predict material phenomena under arbitrary conditions and for arbitrary compositions.

Due to the extensive experience in production of steels, many empirical models have been developed which link the change in a given production parameter, such as the change in concentration of a given alloying element or the change in thermal treatment time, to the effect on a final material property. These relations are simple and easy to implement on the production floor. Unfortunately, these empirical relations are rarely valid for any process conditions or alloys other than the ones for which they were developed. This is, at least in part, due to the fact that these approaches offer little insight into microstructural mechanisms which are involved in bringing about the observed change in the material property.

This situation necessitates a deeper understanding of how an alloy reacts to the drastic thermal cycle imposed by the welding process. In the past, many empirical and semi-empirical models have been developed to capture the microstructure evolution in the heat affected zone of welds. The empirical models required numerous experimental welds and the models remained applicable only for the range of alloys or process conditions studied. Other models have been proposed which take into account diffusion of elements during the transformations. Unfortunately, many of these models only consider the cooling cycle from a given peak temperature. High-temperature phase fractions and stabilities, how
ever, are also a function of the heating rate and the duration at elevated temperatures. Models such as the original Johnson-Mehl-Avrami-Kolmogorov (JMAK) and single grain models\textsuperscript{\textbf{1}, \textbf{3}} offer a more general, theoretical insight into the material evolution. However, they are incapable of capturing the influence of inhomogeneities in composition or the distribution of multiple phases in the initial microstructure. The inclusion of such microstructural detail in numerical models has been computationally prohibitive in the past. Computer technology and programming methods continue to advance, and therefore allow for the development of more detailed material models. In addition, experimental methods to validate phase transformations during the rapid heating and cooling associated with welding have made significant progress in recent years. The measurement of \textit{in-situ}, real-time phase transformations during welding with synchrotron-based x-ray diffraction\textsuperscript{\textbf{7}} is a notable example thereof.

1.5 Motivation and Outline

Considering these recent technological advances and the persistent need to deepen the knowledge of material response to welding, this thesis will present new models and methods for the calculation of microstructural phenomena. The material models are designed in a general, physically-based manner so as to be applicable for a wide range of alloys and arbitrary thermal cycles. The models are detailed to the extent that grain growth, diffusion, nucleation, and phase transformations can be simultaneously and explicitly considered. The general construction of the models enables the future investigation into the influence of alloy composition or varying thermal cycles on final material properties. Also, since the microstructure details such as grain size and phase dispersion are direct results of these simulations, future research can investigate the optimization of alloy compositions and/or welding process parameters to achieve the desired properties of the welded material. If the mechanisms of microstructure evolution are well understood, these simulations can be predictive, avoiding costly trial and error experimental welds.

This thesis continues in chapter 2 with a review of welding models and general material models in the literature. The theoretical background of material modelling is explored in chapter 3, in which microstructural interface mobility and thermodynamic driving forces for microstructure evolution are presented, along with their implementation in phase-field models. Chapter 4 continues the theoretical discussion by addressing the issue of nucleation and introducing a method by which physically-based concepts for nucleation can be incorporated into phase-field models. The microscopic scale concepts of chapter 3 and 4 are elevated to the mesoscopic scale in chapter 5, where a mesh overlay strategy offers a method to calculate microstructural detail on a scale proportional to the weld in a computationally feasible manner. The remaining chapters present case studies on real material and compare the results of the theoretical simulations with experimental results. Grain growth and recrystallization in an austenitic stainless steel as a result of various heat treatments and welding are discussed in chapter 6. Phase transformations that occur during the welding of a low-carbon steel are analysed in chapter 7, in which the simulation results are compared with \textit{in-situ} synchrotron measurements available from the literature. Chapter 8 presents a material model for a dual-phase (ferrite:martensite) steel and scrutinises the agreements and disagreements between simulation and experimental results. Finally, general conclusions are presented in chapter 9.
References


Chapter 2

Development of Modelling Methods in the Literature

2.1 Introduction

Modelling is a powerful method for studying phenomena or processes and gaining an insight which cannot be exposed via traditional experimental methods. The Oxford English dictionary defines a model as

a simplified description of a system, process, etc. put forward as a basis for theoretical or empirical understanding; a conceptual or mental representation of a thing.

Modelling is popular in the field of welding since important mechanisms which determine the final material properties cannot be studied to the desired level of detail experimentally. Given the vast amount of modelling being carried out, it is necessary to clarify the use of some general terms. In this thesis, a modelling approach will refer to a general type or class of modelling technique. Any model belonging to a given modelling approach will follow a similar set of underlying assumptions which, in effect, define the modelling approach. If a model is referred to in this thesis, it is implied that the modelling approach has been refined to a specific case, such as for a certain welding process or a certain material. Modelling, therefore, refers to the refining of general assumptions, the proposal of new conditions for a specific case, and any interdependence these conditions may or may not have with one another. Finally, simulations will refer to results of a model for a given set of parameters.

The modelling of welded material is a most challenging task, both from the materials science aspects and from the mathematical modelling perspective. The process of welding involves thermal gradients of $10^5 - 10^7$ K m$^{-1}$ and heating rates up to $10^2 - 10^4$ K s$^{-1}$, depending on process conditions. In the region next to the weld pool, material phenomena including grain growth, recrystallisation, diffusion, and multiple phase transformations can be activated by these thermal cycles. Since these phenomena are a function of the entire thermal cycle, not just peak temperatures or critical heating rates, it is crucial
that theoretical microstructure models are provided with sufficiently accurate thermal information. Due to the nature of the thermal cycles, thermal calculations must have the spatial resolution required by the temperature gradients and time increments small enough to reflect temporal changes in the thermal field. Equally challenging demands are placed on the microstructure models which need to be able to calculate kinetics and the extents of the aforementioned material phenomena under non-equilibrium conditions. With these requirements in mind, a literature survey of thermal models for the welding process has been made in section 2.2, followed by a review of models for microstructure evolution in section 2.3. Each of these surveys will conclude by highlighting the modelling approaches implemented in the remainder of this thesis.

2.2 Thermal Modelling Methods Reviewed

This review of thermal models in the literature will be divided into analytical models and numerical models. The fundamental difference between the two approaches is that analytical models propose one or more functions which are valid over the entire domain under the prerequisite that a single, closed (non-iterative) solution exists; numerical models discretise complex problems into smaller, interconnected problems that are solved on an iterative basis with the aim of reducing a global residual so as to converge toward a solution. Both methods can be performed manually or by computers.

2.2.1 Analytical Thermal Modelling

Analytical solutions to the complex phenomena in welding processes are few and often limited to considering only certain effects. However, if a solution exists, the analytical methods provide very efficient calculations. Probably the greatest strengths of analytical methods lie in representing heat sources and the temperature field in a transparent manner in which the physical meaning of the parameters is maintained.

The interest in modelling welding phenomena began long before the invention of the modern computer. Rosenthal’s model from 1941 introduced the heat source of an electric arc weld as a moving point source under a quasi-steady state. This gave the simple form

\[ Q_{\text{net}} = \frac{\eta V I}{v_w}, \]  

(2.1)

where \( Q_{\text{net}} \) is the total amount of heat energy that enters the work piece, \( \eta \) is the efficiency, \( V \) and \( I \) are the voltage and current respectively, and \( v_w \) is the welding speed. All material properties were assumed constant with temperature and latent heat was not accounted for. In spite of all the simplifications, the model provided a good temperature field for low temperatures (less than 20% of the material’s melting temperature) and a closed analytical solution was possible.

An improvement came when Pavelic modelled the heat source by a disk with a Gaussian distribution. The Gaussian distribution resembled the actual shape of the arc during welding and, indeed, parameters for this model were drawn from the physical arc. Through the years that followed, these models served as starting points for further models, but these very quickly became too complex for analytic methods.

Nevertheless, analytical methods have continued to be pursued, especially for laser heat sources. Recently, significant progress has been made in adapting analytical models
for computers. Since analytical methods are not dependent on a spatial mesh or time
increments, an arbitrary level of detail can be extracted out of the solutions which are
calculated with near real-time speed. Crafer et al.9 presented a method which makes use
of combinations of simple solutions in an additive superposition of heat conduction prob-
lems to replicate complex heat sources. The drawback is that these models are dependent
on the existence of a unique solution for the entire domain and are thus limited to simple
geometries.

A rather detailed model was proposed for laser sources by Ducharme et al.9 in which the
power absorbed per unit depth was expressed as the product of an absorption coefficient
and the radiative flux across the cross-section of a keyhole. The developers went to
considerable effort to include the effects of laser-metal energy exchange at the atomic level.
including ionic charging, inverse Bremsstrahlung coefficients, and Fresnel absorption via
reflectivity for both the metal and the plasma. It is a pity that with all this attention to
detail, phenomena such as latent heat release and convection were completely neglected.

2.2.2 Numerical Thermal Modelling

The principle need for numerical methods is the solution of complex problems for which
no analytical solution exists. By discretising space (into elements) and time (into time
steps) to a sufficient resolution, numerical methods can solve the differential equations
of state in a piece-wise manner. These piece-wise equations at each element for each
time step are solved iteratively until a solution converges while still satisfying the global
boundary conditions. Naturally, for both the ease of the programmer and the minimisation
of computation time, general methods are usually kept as simple as possible while still
providing opportunity for creative heat source configurations. From the Rosenthal point
source and the Gaussian disk source of Pavelic as starting points, combinations of point
and line,7 and even volume sources have evolved.5

One of the first heat source models to incorporate the weld pool geometry, at least in an
implicit way, was presented by Okada et al.5 The melting temperature, Tm, isotherm did
not form a boundary condition per se in this model, but determined the configuration of
a series of line sources. The positioning of the line sources was the result of optimization
calculations, resulting in some of the lines actually being outside of the weld pool (see
figure 2.1). The model gave satisfactory thermal predictions for lower temperatures, but
it was shown that peak temperatures in the model came short of experimental values by
as much as 150 K.

An example of a Gaussian flux distribution was presented by Nied.10 Here, the distribu-
tion was centred slightly behind the arc position in order to replicate the longer weld
pool tail. No function was derived for the amount of lag, but it was observed that the
offset had a greater influence during higher welding speeds. A creative method aimed at
replicating the weld pool, known as Goldak’s ellipsoid heat source,5 enjoyed particular
success and will be dealt with in section 2.2.3.

A model using the entire weld pool cavity geometry was proposed in 1997 by Wahat
et al.11,12 The model was designed specifically for gas-metal-arc (GMA) welding and split
the heat source into three components, as illustrated in figure 2.2. The first component
represents the liquified filler metal, entering the work piece behind the arc at 2673 K. The
second and third part represent the actual arc energy with an ellipsoid surface source and
a spherical source below the surface. The diameter of the surface and spherical source
are a function of the arc current. The salient difference in this model with respect to earlier models is the explicit use of the weld pool geometry as a boundary condition for the finite element calculations. The method was judged based on its ability to replicate the so-called \( t_{95} \) time\(^*\). For high heat input values, the method had good agreement with experimental temperature measurements, but the performance became less impressive for low heat input values and deviated from experiment by as much as 50%.

For laser welding simulations, simple flux distributions brought good initial results for conduction mode welding\(^1\). Based on energy density measurements, it has been shown that a simple uniform flux, or a ‘top-hat’ flux, is appropriate for fibre-transported laser welding in the conduction mode.\(^{13} \text{ }^{14} \) Takeshita and Matsunawa\(^{14} \) presented a slightly modified, off-centred Gaussian distribution (see figure 2.3). Unfortunately, convective heat transfer in the molten pool was ignored and thermophysical properties of the material were considered temperature independent.

Complexities arise when attempting to model deeper penetration and keyhole welding where, among other phenomena, fluid flow and radiation absorption along the keyhole walls plays an important role. Undaunted, attempts continued to implicitly contain the necessary effects within a heat source model. Sudnik et al\(^{19} \) proposed the use of sub-models whose additive effect would model the complete process. Sub-models for the laser beam, plasma formation, and radiation absorption were proposed. The power of the plasma was deduced from the difference between the total incident laser power and the minimum power required for plasma formation. The radiation absorption sub-model was actually designed to compensate for the multiple reflections off of the keyhole walls, which originated from both the laser and the plasma.

\(^*\)This is the time interval in which the material cools from 800\(^\circ\)C to 500\(^\circ\)C and empirical models use this as a determining factor for the resulting microstructure.

\(^1\)If the energy from the laser beam only causes localised melting of the material, the weld is said to be in ‘conduction mode’. If the energy density of the laser beam is high enough to cause localised boiling, the developing vapour pressure pushes the molten weld pool aside, exposes the underlying material directly to the laser beam, and causes further boiling. This cyclic process drills the weld pool deeper into the material, leading to the designation of ‘keyhole mode’ welding.
2.2. THERMAL MODELS REVIEWED

Figure 2.2: Heat source model using an actual weld pool geometry as a boundary condition.\textsuperscript{12} The parameters $c_f$ and $c_b$ are the dimensions of the front and back of the ellipsoid respectively. The width of the weld pool is given by $\alpha$ and the depth of the spherical source is given by $b$, which is a function of the welding current.

Figure 2.3: Heat source model with off-centred position of the beam.\textsuperscript{14}
Babu et al. employed various strategies to model a heat source for deep penetration welding. Initially, an analytical solution that suggested a spherical heat source coupled with a regular surface disk source was adopted, but results were unsatisfactory. Also efforts to adapt the Goldak method for the conditions in laser welding were unfruitful. The final approach by Babu et al. involved reducing the problem to one dimension by treating the work piece as a stack of thin sheets, as shown in figure 2.4. By using the empirically determined weld pool boundary, the model had a priori knowledge of the melt isotherm and conduction equations calculated the rest of the problem. Temperature profiles were influenced by a manipulable efficiency coefficient in the thermal equations. This efficiency was adjusted for each of the thin sheets with sheets at the top of the keyhole being assigned a higher efficiency than sheets at the bottom. This simplification is questionable and the thin sheet approach is valid only for thin workpieces that are subject to total penetration. Otherwise heat conduction in the vertical direction cannot be neglected.

![Figure 2.4: Heat source model reducing the problem to conduction into the ends of stacked plates.](image)

As mentioned above, complexities of weld pool flow have significant influence on the final thermal profile of a welded work piece and thermal distributions also influence flow patterns. This coupled relation has led to a branch of welding simulations with emphasis on the fluid flow while maintaining comparable models for the heat source. Many models include enhanced conductivity for the fluid region or, as mentioned above in the Goldak model, adapt the shape of the heat source to accommodate the mass flow. A good introduction to the field of fluid flow in welding simulation is given by Zacharia et al.

With a main motivation of generating accurate temperature fields, Mahrle et al. studied mathematical models of the fluid flow in the weld pool. With the use of dimensionless groups including the Péclet, Reynolds and Prandtl numbers and a dimensionless temperature \( \Theta = (T - T_{\text{init}})/(T_{\text{boil}} - T_{\text{init}}) \) with \( T_{\text{init}} \) and \( T_{\text{boil}} \) the initial and boiling temperatures respectively, the Navier-Stokes equations could be solved. Since the position of the melting front boundary was treated as an unknown, the solution was not closed and had to be solved iteratively by means of the Gauss-Seidel method with over-relaxation. Simulated temperature profiles had good quantitative agreement with both thermocouple and infrared imaging data in high temperature regions, but exhibited larger deviation...
2.2. THERMAL MODELS REVIEWED

from the measurements in low temperatures regions. This was blamed on poor accuracy of the thermocouples and thermography at low temperatures.

Fuhrich et al.\textsuperscript{21} considered the inner wall of the keyhole as a tapered cylinder with a fixed geometry. The boundary conditions were then such that the temperature along the entire inner surface of the keyhole was maintained at the boiling temperature. Convection due to buoyancy was entirely neglected under the assumption that surface tension gradients with respect to temperature played a much larger role. The weld pool geometry was simply given as a result of the melting temperature isotherm. This work showed great insight into flow patterns within a keyhole weld pool and how they vary with depth in the work piece as a function of surface tension, an example of which is shown in figure 2.5. The fixed keyhole geometry simplified calculations significantly, but could misrepresent the weld pool shape.

![Figure 2.5: Cross sections of the weld pool at increasing depth from the top surface showing the direction and magnitude of flow for negative $\partial\gamma/\partial T$.\textsuperscript{21}](image)

There are very few models that consider both the keyhole and weld pool geometry as free moving surfaces, most likely due to the immense computational effort required for such a simulation. Ki et al.\textsuperscript{22} proposed such a model, using a Gaussian distribution for thermal energy input with a constant beam radius in the depth of the work piece. The actual energy entering the work piece was modelled as the total power from the laser minus energy lost to evaporation and radiation. The main thrust of the model is capturing the free surface movement of the inner keyhole wall (as opposed to the fixed geometry proposed by Fuhrich et al.\textsuperscript{21}), so the surface subject to heat input is determined by what particular surface finds itself under the laser at a given point in time.

The immensity of this problem should not be underestimated. A grid spacing of less than 50 $\mu$m and time steps of 10$^{-9}$ seconds require solving for approximately 10$^{10}$ degrees of freedom for only one second of simulated welding. The code was parallelized and optimized for super-computing platforms, meaning that even for today’s researcher these
Figure 2.6: Flow patterns in a free surface simulation of the keyhole and weld pool.22
methods come at a tremendous computational cost.

Further models for simulating the temperature profiles during welding have been reviewed by Mackwood and Crafer. They thermal models implemented in this thesis are covered in the following section.

2.2.3 Implemented Thermal Models

In his original heat source model, Goldak et al. proposed a three dimensional distribution of the heat flux resulting from a welding arc, divided into leading and trailing distributions. The flux distribution was described by

\[
q_i(x, y, z) = \frac{6}{\alpha \beta \gamma \pi c^2} \cdot \exp \left( \frac{-3 x^2}{a^2} \right) - \exp \left( \frac{-3 y^2}{b^2} \right) - \exp \left( \frac{-3 z^2}{c^2} \right)
\]

(2.2)

where the subscript \( i \) indicates the front or rear of the distribution, \( q_i \) is the flux, \( Q \) is the welding arc power defined by \( \eta V I \), where \( \eta \) is the energy transfer efficiency coefficient and \( V I \) is the product of the voltage and current. The spatial coordinates are given by \( x, y \) and \( z \) with \( y \) the weld direction and \( z \) the depth of the welded specimen. The parameters \( a, b, \) and \( c \) define the flux distribution width, length, and depth respectively. The division of the total welding power to the front and rear of the distribution is regulated by \( f_i \). It is unlikely that the heat input distribution in a physical weld is directly tied to the melt line or that energy flux behind the arc is higher than in front. It is more probable that this modelled flux distribution makes up for effects of flow in the weld pool due to convection, surface tension gradients and Lorentz forces. Nevertheless, calculated thermal profiles using the Goldak volume flux have agreed well with measured temperatures and the computational effort is lower than that necessary for other models in the literature. In this thesis, Goldak’s thermal model has been adapted to a double-ellipsoid surface flux via

\[
q_i(x, y) = \frac{6}{\alpha \beta \gamma \pi c^2} \cdot \exp \left( \frac{-3 x^2}{a^2} \right) - \exp \left( \frac{-3 y^2}{b^2} \right)
\]

(2.3)

in which the trailing half ellipsoid was set longer and the width of both the front and back ellipsoid was determined experimentally as the width of the weld bead. A typical flux distribution is shown in figure 2.7.

This flux distribution was programmed into a user-subroutine and implemented in a commercial finite element package. Temperature dependent material properties such as conductivity and heat capacity were taken from the literature. An enhanced thermal conductivity was used above the melting temperature to compensate for mass transport in the weld pool.

Although models for laser welding were investigated, the heat affected zone in common steels with standard laser welding process parameters was extremely small. The material modelling, which forms the bulk of this thesis, is general in construction and can be used in the simulation of material response to arbitrary thermal cycles. However, the most information was to be gained by studying and simulating welding processes which produce larger heat affected zones. Therefore, the thermal modelling in this thesis is primarily performed with the adapted Goldak surface flux model for arc welding processes.
2.3 Microstructure Modelling Methods Reviewed

2.3.1 Implicit Microstructure Modelling

This section deals with microstructure modelling methods which do not explicitly recover the microstructure morphology as part of the solution. A common output is then a phase fraction or average grain size for the calculated domain. A simple adaptation of these modelling methods is to consider multiple, interconnected domains, which can then reflect gradients of certain quantities. Although many of the models in this section are based on simplifications of morphological features, such as interlamellar spacing or particle radius, these features are not mapped back into any representation of the intermediate or final microstructure. Nevertheless, many classic modelling approaches fall under this classification and still offer valuable insight into the mechanisms of microstructure evolution during welding.

Empirical Models

Before the days of large numerical simulations, researchers were forced to use other methods for analysing welded microstructures and developing their theoretical models. A logical first approach was to develop empirical models based on a multitude of experiments, including welding and controlled heating/cooling experiments. Some of these methods are still being used today, offering a great reduction in computation time, while other empirical methods led to errors that are no longer acceptable.
2.3. MICROSTRUCTURE MODELS REVIEWED

A popular empirical modelling method was to use Continuous Cooling - Time (CCT) diagrams to determine final microstructures. Here, a series of continuous cooling experiments are conducted and the final microstructures are examined. From the data, cooling trajectories can be plotted on a temperature-time graph with the trajectories going through regions of phases which can be expected in the final microstructure. Models based on this method use data from a thermal model as input to compare with the CCT diagram. Commonly, these models employ Scheil’s additivity to predict a final phase fraction as a function of the amount of time spent in any given temperature range.\(^{25}\)

Meltzer\(^{27}\) suggested a method using CCT diagrams and experimental grain size measurements as input for a flowchart of microstructure evolution in welded titanium. A finite element model was constructed to calculate the thermal history. Each node possessed a data structure, called a ‘frame’, which in turn was described by a substructure, labelled an ‘instance’. A frame for a given node could, for example, contain instances of morphology descriptions (such as equiaxed grains), a phase fraction of \(\alpha\), grain size, and a temperature \(T\). In each time increment, the data frame was subject to series of logic filters to alter the properties at the node. A rather complex flow chart was developed specifically for the Ti-6Al-4V alloy and, although empirical grain size and phase fractions were calculated, the model showed no capacity for reflecting compositional change and was limited to the narrow range of cooling rates in the available CCT diagram.

CCT diagrams have also been used to calculate some characteristics of final microstructures in welded steel. However, Stadtaus et al.\(^{28}\) warned that this method is not only composition dependent, but must also reflect a dependence on the peak temperature reached. Simply representing the microstructure as total austenite above \(A_3\) is not sufficient, since above this temperature the grains of austenite continue to grow. Larger and more stable grains of austenite cause a delay of the ferrite nucleation upon cooling, which cannot be neglected. This produces a CCT diagram that is shifted to the right for higher peak temperatures, shown in figure 2.8. Furthermore, Stadtaus observed that extrapolating a given CCT diagram to accommodate for the higher cooling rates in laser welding led to errors in predicted final phase fractions of up to 20%.

Work has been done on neural network models that interpolate CCT diagrams for compositions that fall between compositions with known CCT diagrams.\(^{29}\) Unfortunately, the same shortcomings in the CCT data identified by Stadtaus would be included in the input for this predictive system as well.

Another class of empirical models found in the literature are based on what has become known as the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation, derived from the independent work of Johnson and Mehl,\(^{30}\) Avrami\(^{31}\) and Kolmogorov.\(^{32}\) The equation was derived to describe isothermal phase transformations, with the phase fraction as a function of time being expressed as

\[
f_p = 1 - \exp \left[ - (Kt)^n \right],
\]

where \(f_p\) is the fraction of the growing phase (here \(\gamma\)), \(t\) is the time, \(n\) is the growth-mode exponent, and \(K\) is a parameter of which the temperature dependence is defined by

\[
K = K_o \exp \left( \frac{-Q_{ne}}{RT} \right).
\]

\(K_o\) is a pre-exponential factor, \(Q_{ne}\) is the activation energy for both nucleation and growth, and \(R\) and \(T\) are the universal gas constant and temperature respectively. As the theory
Figure 2.8: Continuous Cooling - Time diagram reflecting the shift due to different peak temperatures. If the cooling rate trajectory goes through the zone marked with M, the resulting microstructure has martensite. F, P, B represent ferrite, pearlite, and bainite respectively. Cooling time $\Delta t_{85}$ is in reference to the time taken for the material to cool through the critical temperature range for steels of 800°C to 300°C.

was originally presented, a random distribution of nuclei is assumed along with a constant velocity of the growing phase front. The exponent $n$ was intended to describe the type of growth that the nucleating phase experienced: $n = 3$ for isotropic, spherical growth, $n = 2$ for plate-like, 2 dimensional growth, and $n = 1$ for acicular, needle-like growth. $K_0$ was originally proposed as a function including the nucleation density and isokinetic growth rate. Already in the sequel to the original paper, Avrami31 showed that $n$ could actually be any real number between 1 and 3 for transformations in which a combination of acicular, plate, and polyhedral growth occurred. The JMAK equation has also been adapted to the non-isothermal case by representing a given thermal cycle by a series of isothermal steps and then applying Scheil additivity.

For the complex conditions of welding, Elmer et al.31 attempted to match experimental results to JMAK-calculations by fitting $K_0$, $n$, and $Q$. However, the underlying assumptions in the JMAK equation are too stringent: during welding, the approximation of phase fronts moving with a constant velocity is quite crude. Although the JMAK equation can be forced to fit experimental transformation curves (since they all have a sigmoidal character), it does not mean that the physical prerequisites stipulated in the original work31 have been met. Through the extensive effort to manipulate $K_0$, $n$, and $Q$ in order to match $f_T$ to experimental measurements, the physical meaning of the parameters became clouded.

**Diffusion-Controlled Transformation Models**

In many phase transformations, the diffusion of a given species can be slower than the other mechanisms in the transformation (such as atomic re-arrangement) and thereby becomes the rate-controlling process. Many models have been proposed to simulate diffusion-
controlled phase transformations, dating back to the classic work by Zener. Although the early models were not constructed specifically for the welding process, many of the principles are universally applicable. In more recent work, Lee et al. combined classical nucleation theory and diffusion equations to simulate the $\gamma \rightarrow \alpha$ transformation in Nb-containing steels. Diffusion equations were adapted for curved surfaces, due to the assumed average elliptical grain shape and the models produced Time-Temperature-Transformation (TTT) diagrams for a small range of alloys. Reed et al. used standard diffusion equations with the assumption of local equilibrium at the phase interface. Morphology was reduced to one dimensional lengths for cementite, austenite, and ferrite. Output for this model included TTT diagrams and simulations of dilatometry curves. A model has also been proposed for an arbitrary system with multiple diffusing species and multiple phases. While the derivation of thermodynamic driving forces was more rigorous than in the aforementioned models, the model was constructed on the assumption that capillarity was negligible which, in other words, limits the model to only near-planar interfaces.

An important subclass of the representative microstructure models using diffusion is that of models which also consider interface mobility as a kinetics determining mechanism. Svoboda et al. considered multiple diffusion fields, a finite interface mobility, and even influences of lattice strains to produce an analytical expression for the interface position. Even though the model was later applied to the Fe-rich corner of the Fe-Cr-Ni-C system, the assumptions that were required to attain an analytical solution limited the model to one dimensional problems. Sietsema and van der Zwijg produced a more general model to capture so-called mixed mode transformations. Minor adaptations to their presented model could account for soft impingement of diffusion fields in 2 or 3 dimensions, but were not implemented. The model was, however, limited by the fact that interfacial energy was neglected which plays an important role in the transformation directly after nucleation. These considerations will be treated in more detail in chapters 3 and 4.

The literature also contains several variants of diffusion models aimed specifically at representing phase transformations during welding. These models are often highly customized to dealing with a specific alloy, either in composition or in microstructure class. Katzbarov et al. proposed a model for the $\beta \rightarrow \alpha$ transformation in the Ti-6Al-4V alloy. In this alloy, the morphology of the $\alpha$-phase is dependent on cooling rates. A slow cool produces plate-like $\alpha$-phased regions while a quench results in fine needles of $\alpha$. The governing process is the diffusion of vanadium because of its low mobility. The model was then developed within the finite element method to represent the different phases based on the diffusion equations of vanadium. Since the approach was based on classical phase transformation models that explicitly trace the moving phase interface, the standard Lagrangian formulation would have caused highly localized distortion of the mesh and lead to numerical instabilities. Therefore, the Eulerian setting was implemented, but the change in setting did not circumvent the special treatment needed for tracking the moving free surface. The mobile phase front was handled by using volume elements that ‘filled up’ with $\alpha$-phase as the diffusion progressed. Further numerical juggling was needed to precisely define the interface’s location since many neighbouring elements could be partially filled. The method’s success was limited to cooling rates between 5 K s$^{-1}$ and 50 K s$^{-1}$ in the temperature range of 1025 - 1275 K.

Internal state variables is a concept that has been used in computational mechanics for quite some time to describe a material. These state variables can be used to describe, for example, the fraction of the total strain that is plastic strain. This then enables
functions of hardening to be calculated without having to store the entire deformation history. Similarly, state variables in a microstructure model can be used to describe the condition of a volume element without storing the entire thermal history. Each time step implicitly carries the thermal history along as a result of the updated microstructure. It should be noted that this approach also maintains path dependency, an important factor when handling microstructure simulations in a welding application where both the effects of heating and cooling influence the resultant microstructure. Hemmer and Grong adapted the considerations of state variables to the prediction of microstructure in welded dual phase steels. The model captured the dissolution of austenite upon heating, grain growth of the δ-ferrite, and the decomposition of the δ-ferrite back into austenite. Above the computational advantages of the state variable approach, Hemmer et al. made assumptions on the microstructure and reaction order to further simplify the simulation. The dual phase stainless steel microstructure was reduced to parallel and alternating lathes of austenite and ferrite and, utilizing symmetry, this reduced the simulation to a one-dimensional diffusion problem as shown in figure 2.9. Also, it was assumed that the phenomena associated with the phase transformations occur strictly in series (eg. all the austenite is decomposed into δ-ferrite before any grain growth occurs). Another assumption was that the dissolution of austenite in the alloys studied is governed by the diffusion of nitrogen, which then obeyed Fick’s law of diffusion. The low carbon content (0.02 wt%) was considered negligible next to the nitrogen content of the alloys (0.12, 0.18, and 0.28 wt%).

Figure 2.9: Concentration profile for nitrogen during austenite dissolution.

The solutions for the diffusion equations assumed local equilibrium at the interfaces and the transformation is calculated based on Scheil additivity, which basically breaks down a thermally dependent problem into a series of small isothermal steps. In each step, the transformation rate is assumed to be governed by diffusion (of nitrogen). The model presented a computationally robust and efficient method for representing the microstructure in duplex steels. Unfortunately, some of the assumptions that produced such an efficient calculation also restrict the applicability of the model. The banded microstructure assumption does not permit a general microstructure representation and the assumption of reactions occurring purely in series is also not totally valid. Also, the model used a
2.3. MICROSTRUCTURE MODELS REVIEWED

Rosenthal heat source, known to produce inaccuracies in the high temperature regime. Nevertheless, the merits of the model were not to be overlooked and the model was modified by Myhr et al. to predict microstructure in Al-Mg-Si alloys. Here, the banded structure model for duplex steels was converted to assumptions of spherical precipitates. With this assumption, the problem could once again be reduced to a one-dimensional diffusion problem. Results from the Myhr and Grong microstructure model were then imported into a commercial finite element package to determine residual stresses and strains and predict mechanical properties and fracture behaviour. This modelling approach was continued by Zhang et al. in the modelling of ferrite formation in duplex stainless steel, in which diffusion of nitrogen was seen as the rate controlling process. Again, the microstructure morphology was reduced to one dimension but effects of a non-uniform starting microstructure were incorporated by considering an alternating series of δ- and γ-phase grains. An interesting feature of the model was the adaptive mesh in which a given grid point defined the δ : γ interface and as the interface moved, grid points behind and in front of the interface shifted to maintain an even spacing within a phase. The model was compared with in-situ synchrotron diffraction measurements in which only the δ-ferrite formation was modelled, leaving the reversion to austenite upon cooling untouched.

Another group of researchers adapted the concept of internal state variables for the solidification and microstructure of two aluminium alloys. For the solidifying weld pool, attempts were made to use Scheil’s principle of additivity, but these were unsatisfactory. A method which was seen as more capable of representing the diffusion flux was to treat the solidification interface as being in local equilibrium. The validity of these assumptions is questionable, but it did allow numerical solution of the diffusion flux equations. The dendritic growth of the α-phase was represented as a diffusion problem over half the distance to the neighbouring dendrite. Constant cooling rates and initiation of eutectic phase between the dendrites were further assumptions. This geometrical reduction of the dendritic growth strongly resembled the banded structure assumptions from the duplex steel model from Hemmer and Grong. For prediction of the dissolution and precipitation of β’ (Mg2Si), the Hemmer-Grong model was quoted as an adopted method. The model also adopted the principles of additivity to predict softening and hardening, presumably by associating an empirical hardness value with a given phase and interpolating based on the fraction of each phase present.

Another diffusion model targeted toward austenite decomposition proposed idealizing the material as filled with spherical cells having a core of cementite and shell of ferrite. These cells were assigned a beginning carbon content, $c_{\text{total}}$, based on alloy data. The initial radius of the cementite core, $R_0$, was experimentally determined and the total cell radius followed from the mass balance

$$\int_0^R c_{\text{total}}r^2 \, dr = \int_0^{R_0} c^\delta r^2 \, dr + \int_{R_0}^R c^\gamma r^2 \, dr,$$  \hspace{1cm} (2.6)

with carbon contents of cementite and ferrite determined from the phase diagram. Diffusion was then calculated according to literature values for activation energies and diffusion constants. This model also attempted to represent the fraction of martensite by switching calculated austenite over to martensite upon cooling. Hardness values were predicted based on pure empirical relations. Since the model contains one cementite and one ferrite region, the assumptions of the homogeneous distribution of nuclei and site saturation nucleation (all nucleation occurring simultaneously) are implicitly made. These assumptions.
coupled with the fact that the austenite formation is not considered, limit the model’s applicability in the simulation of transformations during welding.

2.3.2 Explicit Microstructure Modelling

This section reviews microstructure models which inherently reproduce features of the microstructure morphology as part of the solution. These methods are generally much more computationally intensive than the models discussed in section 2.3.1, which explains the fact that most of these methods have only enjoyed recent success, concurrent with the increase in modern computing power. Most of these methods are adaptable to calculate in 2 and 3 dimensions, with the only limitation being those of the employed computational facilities.

Monte Carlo Methods

Monte Carlo (MC) methods can be used for detailed analysis of microstructure evolution. The method operates with a fixed grid of points, each being assigned an orientation. Grains are then determined by clusters of points with identical orientations. Although the variation in orientation in real crystals is infinite, it can be shown that allowing a large finite number of orientations has limited influence on grain growth simulations. Sista and DebRoy set the number of possible orientations to 48 with favourable results. To simulate grain growth and recrystallization, grid points are given a probability of changing orientation within a time step. This probability of orientation change is defined as

\[ p = \begin{cases} 1 & \text{for } \Delta E \leq 0 \\ \exp\left(-\frac{\Delta E}{kT}\right) & \text{for } \Delta E > 0 \end{cases} \]

(2.7)

where \(\Delta E\) is the change in energy due to change in orientation, \(k\) is the Boltzmann constant and \(T\) is the temperature. In a 3-D simulation with a regular orthogonal grid, a point will have 26 first-, second- and third-nearest neighbours. Thus, the change in energy due to orientation change is given by

\[ \Delta E = J \sum_{i=1}^{26} (\delta s_i s_o - \delta s_i s_n) \]

(2.8)

where \(J\) is a positive constant which determines the scale of the grain boundary energy. \(s_o\) is the original orientation of the point’s nearest neighbours, and \(s_n\) is the new orientation number. In this model, grain boundary energy is treated as isotropic and, in its current form, is only valid for grain growth. For other important phenomena, such as recrystallisation or phase transformation, additional terms would be needed in equation 2.8. This particular model also reported no coupling to diffusion equations, whereas other MC models have considered diffusion. Still other MC models have been developed to calculate the phase changes in the welding HAZ, such as proposed by Yang et al. and Shi et al.

However, the greatest shortcoming of all MC models is the fact that there is no inherent coupling to real time in the calculations. Considerable effort has been spent...
2.3. MICROSTRUCTURE MODELS REVIEWED

In establishing this connection via empirical relations to grain growth laws. The classical isothermal grain growth law can be stated as

\[ L^n - L_0^n = K^G t \exp \left( \frac{-Q_G}{RT} \right), \]  \hspace{1cm} (2.9) \]

where \( L \) and \( L_0 \) are the current and original grain size respectively, \( n^G \) is the growth exponent\(^1\), \( K^G \) is a material constant, \( t \) is time and \( Q_G \) is the activation energy for grain growth. The current grain size in a MC simulation can be expressed as

\[ L = K^G_1 \lambda (t_{MC})^{n^G_1}, \]  \hspace{1cm} (2.10) \]

where \( K^G_1 \) and \( n^G_1 \) are model constants, \( \lambda \) is the grid spacing, and \( t_{MC} \) is the MC dimensionless time. By substituting equation (2.10) into (2.9) and integrating it over an entire thermal cycle via summations of the grain growth in short real-time intervals, the following relationship is deduced

\[ (t_{MC})^{n^G} = \frac{L_0^{n^G}}{(K^G_1 \lambda)^{n^G}} + \frac{K^G}{(K^G_1 \lambda)^{n^G}} \sum \Delta t_i \exp \left( \frac{-Q}{RT} \right), \]  \hspace{1cm} (2.11) \]

As can be seen, the relation between real time \( t \) and simulation time \( t_{MC} \) in MC simulations is dependent on the assumption that the material follows the classical grain growth law.

Since the grain growth law is derived for isothermal conditions, it is questionable if it can be used as the basis for coupling measurements of time in welding simulations.

**Cellular Automaton Methods**

Cellular automata (CA) is another tool used to perform micro-scale simulations. These simulations define individual lattice points that are described by a state variable. This state variable takes on a value from a discrete set of states. Evolution of these states is done through probabilistic transformation rules, which are also known as switching rules. These rules are functions of the states in neighbouring points, the influence of which grows inversely with the distance (see figure 2.10). The model was originally developed in the 1960’s for simulating population evolution.

In material simulation, the lattice points of the CA method often coincide with actual crystal lattice points in the material. It is therefore essential that common transformation rules that apply to different time scales (e.g. recrystallization and recovery or bulk diffusion and grain boundary diffusion), both of which are included in the model, be subject to a scaling to achieve commonality over the entire system.\(^2\) For grain boundary motion during recrystallization, Raabe\(^3\) suggests a transformation rule

\[ \dot{x} = n \nu_0 \lambda_{gb} \exp \left( -\frac{\Delta G + \Delta G_{gb}/2}{kT} \right) \exp \left( -\frac{-\Delta G - \Delta G_{gb}/2}{kT} \right), \]  \hspace{1cm} (2.12) \]

where \( \dot{x} \) is the grain boundary velocity, \( \nu_0 \) is the Debye frequency, \( \lambda_{gb} \) is a ‘jump width’ through the grain boundary, \( c \) the concentration of grain boundary vacancies (in the CA

\(^1\)In the classical treatment, \( n^G = 2 \) is often used. However, this has been shown to be a function of the material and the temperature.\(^4\)
simulation these could be considered as ‘shuffle sources’), $\mathbf{n}$ is the normal to the grain boundary segment, and $\Delta G$ and $\Delta G_i$ are the enthalpy of motion through the interface and enthalpy of transformation respectively. This compilation of exponential functions produces a quasi-Heaviside function that steps the state variable of a particular lattice position. Raabe also showed that reformulating the above switching rule in terms of total entropy and enthalpy converts the ‘jump width’ to the Burgers vector.

Other CA models have been applied to the simulation of phase transformations. Kumar et al.\textsuperscript{59} modelled the nucleation and growth of ferrite upon cooling austenite on the scale of a single grain. Ferrite nucleation occurred at pre-determined nodes in the CA mesh with a nucleation rate that was assumed to have a Gaussian distribution over the nucleation temperature range. Ferrite then grew based on a diffusion controlled rate, assuming equilibrium concentrations of both ferrite and austenite as derived from a linearised Fe-C equilibrium phase diagram. This approach was refined and expanded by Zhang et al.\textsuperscript{59} who considered a 200 x 200 grid (corresponding to 125 $\mu$m square). Nucleation occurred via probabilistic switching of grid points on the austenite grain boundaries with a subtle difference to the model presented by Kumar et al.\textsuperscript{59} Zhang et al. borrow an idea proposed by Jacot et al.\textsuperscript{19} in that nucleating grid points also convert neighbouring grid points to $\gamma : \alpha$ interface points. This moderates the gradients in the diffusion field calculations. However, two important factors detract from these models. Firstly, interfacial energy is neglected and this plays an important role in initial transformation kinetics. Secondly, these models assume that grid points assigned as austenite have the equilibrium composition of austenite, just as ferrite grid points have the equilibrium composition of ferrite. This means that concentration gradients across a grain are ruled out and that the models are limited to very low cooling rates where complete homogenisation can be assumed.
Phase-Field Methods

Microstructure modelling in this thesis will make use of the phase-field method (PFM). This sub-section is intended to give a brief historical background of the method and introduce the general concepts. The unique aspects of the phase-field models used in this thesis will be presented in section 2.3.3.

The core of the phase field method is the assumption that a state variable is defined over the entire computational domain. This state, or phase-field variable can be dependent on conserved variables, such as composition, or on non-conserved variables, such as orientation, long-range order, or lattice structure. Rather than tracking a sharp interface of zero thickness, a diffuse border is represented as the region where the state variable can vary between two extreme values (usually 0 and 1, representing phase α and phase β respectively). As a region’s state variable changes, the front of the phase boundary is implicitly given, avoiding the difficulties of tracking the interface and the quantities that would have to pass through it. In the past, the rigors of defining a variable over the entire domain have made this approach computationally prohibitive. Ever increasing computational power has made it feasible to use theoretical state variables, which consider changes in chemical, crystallographic, and structural fields. These state variables appear frequently as ‘phase-field variables’. The most versatile approaches are the Cahn-Hilliard and Allen-Cahn kinetic phase-field models, which can be regarded as metallurgical derivatives of the theories from Onsager and Ginzburg-Landau.48

The original Ginzburg-Landau model was directed at calculating electro-magnetic second-order phase transition phenomena. Cahn and Hilliard adapted these equations to represent the interfacial free energy of a nonuniform system.49 A distinguishing characteristic recognized by Cahn and Hilliard was that the model did not use an a priori value for the interface thickness between two phases, but rather allowed this to be the solution of an equilibrium equation for the whole system. The approach used a diffuse interface
that grew in thickness and approached an infinite thickness as both phases approached the same composition (i.e. no interface). Although the model represented the free energy distribution as a function of the composition, it was shown that this method could be applicable for any internal variable and even for multiple internal variables. The pivotal equation of the model split the free energy of the system, $\mathcal{F}$, into the sum of the internal free energy of a uniform system and the square of the gradient of a continuous internal variable. The original form of the Cahn-Hilliard equation.

$$\mathcal{F} = N_V \int_V \left[ f_0 + \Pi (\nabla c)^2 + \ldots \right] dV ,$$  \hspace{1cm} (2.13)

used the molecular free energy with $N_V$ as the number of molecules per unit volume, $V$ as the volume of the system, $f_0$ as the free energy in the uniform solution, $c$ as the concentration and $\Pi$ as a differential operator, which, after reductions for crystal symmetry, reduces to

$$\Pi = -\frac{\partial^2 f}{\partial c \partial^2 c} + \frac{\partial^2 f}{(\partial \|\nabla c\|)^2} .$$  \hspace{1cm} (2.14)

The particular form of the gradient term was given by a standard Taylor expansion of the energy about the interface. Since this value must be invariant with respect to the direction of the gradient, only even-powered gradients were used. Analyzing the shape of the $\Delta f$ function (see figure 2.12a), Cahn and Hilliard concluded that the shape of the composition profile must be sigmoidal (figure 2.12b) with the solution in the range of a critical temperature and about the interface of

$$\left( \frac{\Delta c}{\Delta c_e} \right)_{T \to T_c} = \tanh \left[ \frac{\beta (T - T_c)}{2\Pi} \right]^{\frac{1}{2}} x ,$$  \hspace{1cm} (2.15)

where $T_c$ is the temperature at which both phases reach the same critical composition, $c_c$, and $\beta$ is a differential operator between the free energy and temperature.

![Figure 2.12: The free energy across a phase interface (left) and the compositional profile across the interface (right) from the Cahn-Hilliard equation.][1]

With continued interest from other researchers, the modelling approach developed into what has become known as the phase-field method. Caginalp showed that as the

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[1]: Figure 2.12: The free energy across a phase interface (left) and the compositional profile across the interface (right) from the Cahn-Hilliard equation.
2.3. MICROSTRUCTURE MODELS REVIEWED

thickness of the interface approaches zero, the equations can reduce to the classical Stefan problem. The dependent variable of composition was shown to be replaceable with the general phase-field variable, φ, which in the specific case can still be reduced to φ = c. The free energy density thus becomes a function entirely of temperature and the phase-field, which, motivated by the Gibbs free energy shown in figure 2.12a, was usually assumed to have the so-called ‘double-well’ dependence on φ, shown in figure 2.13. For clarity, the free energy density function, f, can be presented as $f = f(g, p)$, where $g = g(\phi)$ is the double-well potential and $p = p(\phi)$ acts as an interpolation function between the free energy in the bulk of the two phases.

![Double-well form of free energy density](image)

Figure 2.13: Double-well form of free energy density. Representation here is for the range $\phi = 0 \ldots 1$, but it can also be constructed for the range $\phi = -1 \ldots 1$.

There is no unique solution for $g(\phi)$ or for $p = p(\phi)$, but if the range for $\phi$ is between 0 and 1, the functions $g(\phi) = \phi^2(1 - \phi)^2$ and $p(\phi) = \phi^3(6\phi^2 - 15\phi + 10)$ could be used.\(^{51}\) It should be pointed out that $g'(\phi)$ should have the feature of $\partial f / \partial \phi = 0$ for the extreme values of $\phi$ (here 0 and 1) to ensure stability of the phases. It has been shown that a quintic function for $p(\phi)$ is the simplest form that preserves the double-well for arbitrary temperatures.\(^{62}\) The construction of the actual free energy density function can then proceed in several ways. If limited thermodynamic data is available, an intuitive approach is to use the interpolation function between known values of the free energy of the phases under consideration. Given free energy values for the α- and γ-phases of a pure substance $A$ ($f_A(\phi, T)$ and $f_A(\phi, T)$ respectively), $f_A(\phi, T)$ could take the form

$$f_A(\phi, T) = (1 - p(\phi)) \cdot f_A(\phi, T) + p(\phi) \cdot f_A(\phi, T) + W_A \cdot g(\phi), \quad (2.16)$$

where $W_A$ is the energy barrier between the phases preventing spontaneous phase transformations. To incorporate the effects of an alloying element, the free energy density function is adapted once more. For clarity, composition will be represented by $c = c_B$ as

\(^{51}\)Other models adopt a double-obstacle potential, with a simple quadratic function for $g(\phi)$ for $-1 < \phi < 1$ and $g(\phi) = \infty$ for $|\phi| > 1$
the ratio of $B$ in the alloy, but it can be shown that composition can also be represented by a second phase-field variable. The free energy density function then takes on the form

$$f(\phi, c, T) = (1-c)f_A(\phi, T) + c f_B(\phi, T) + R' T |(1-c) \ln(1-c) + c \ln c| + c(1-c) \left\{ \Omega_\alpha [1 - p(\phi)] + \Omega_\gamma p(\phi) \right\},$$

(2.17)

where $R'$ is the universal gas constant normalized per unit volume. $\Omega_\alpha$ and $\Omega_\gamma$ are the regular solution parameters of the $\alpha$- and $\gamma$-phases.\(^{(36, (61)}}\)

If, on the other hand, a sufficient thermodynamic database is available, the free energy density function can be immediately constructed according to

$$f(\phi, c, T) = \left[ (1-c) W_A + c W_B \right] g(\phi) + \left[ 1 - p(\phi) \right] f^\alpha(c, T) + p(\phi) f^\gamma(c, T).$$

(2.18)

The phase field itself is assumed to evolve according to

$$\dot{\phi} \propto \mathcal{L} \left( \frac{\partial F}{\partial \phi} \right),$$

(2.19)

where $\mathcal{L}$ is a differential operator. Wheeler et al.\(^{(35)}}\) proposed a modified free energy functional integrated over the entire domain, $\Omega$,

$$\mathcal{F} = \int_\Omega \left[ f(\phi) + \frac{\epsilon^2}{2} \| \nabla \phi \|^2 \right] d\Omega,$$

(2.20)

and that the differential operator in 2.19 is simply a phase-front mobility term, $M_1$, shown by

$$\frac{\partial \phi}{\partial t} = M_1 \frac{\partial \mathcal{F}}{\partial \phi}.$$  

(2.21)

After integration and requiring $\phi \to 1$ as $x \to -\infty$ while $\phi \to 0$ as $x \to +\infty$, the solution

$$\phi(x) = \left[ 1 + \exp \left( x \sqrt{\frac{W}{2\epsilon^2}} \right) \right]^{-1}$$

(2.22)

followed, with $W$ and $\epsilon$ being material constants related to the excess free energy of the interface region and the thickness of the interface itself. Wheeler et al gave considerable effort in relating constants in the phase-field model, which were previously seen as rather arbitrary and leading the phase-field model towards an exercise in parameter fitting, to measurable physical properties of a material. Furthermore, they also included a linear interpolation of the specific internal energy for the release of latent heat during a phase transformation.

Phase field models have seen application in various branches of microstructure modelling. Significant work has been done in the area of grain growth simulations,\(^{(54, 56)}}\) spinodal decomposition,\(^{(60)}}\) martensitic transformations in ceramics\(^{(61)}}\) and shape memory alloys,\(^{(58, 69)}}\) and solidification.\(^{(61, 70)}}\) Detailed reviews of the method and various applications can be found in the literature.\(^{(38, 41)}}\)
2.3.3  Implemented Microstructure Model: Multi-Phase Phase-Field

The modelling of microstructure evolution in this thesis consists of many material submodels incorporated into multi-phase phase-field models. The original concept for a phase-field model with an arbitrary number of phases was proposed by Steinbach et al.\textsuperscript{73} For $N$ phases, the approach then becomes to define an array of $\phi_i$ going from $1 \ldots N$. Considering a variation of $\phi = 0 \ldots 1$, a crucial condition becomes

$$\sum_{i=1}^{N} \phi_i = 1 ,$$

(2.23)

which is enforced at each grid point. A proposed adaptation to the free energy density function\textsuperscript{61} is

$$f = \sum_{j,k(i<j<k)} W_{jk} \left\{ \alpha \phi_j^2 \phi_k^2 - \frac{m_{jk}}{3} (1 + \phi_j^3 + 3\phi_j^2\phi_k - 3\phi_j\phi_k^2 - \phi_k^3) \right\} ,$$

(2.24)

with $W_{ij}$ being a symmetric matrix carrying the values of the energy barriers and $m_{ij}$ being an antisymmetric matrix relating the thermal driving force based on $\Delta T$ from the equilibrium temperature of the interface. Inserting this into the free energy functional, such as in 2.20, yields

$$F = \int_{\Omega} \left\{ f(\phi_1, \ldots, \phi_N) + \sum_{j,k(i<j<k)} \left[ \frac{c_{jk}}{2} \| \phi_j \nabla \phi_k - \phi_k \nabla \phi_j \|^2 \right] \right\} d\Omega ,$$

(2.25)

with $c_{jk}$ now being a symmetric matrix of gradient coefficients (as opposed to the single value in earlier treatments). MICRESS\textsuperscript{\textregistered}, a general, multi-phase phase-field code, solves these equations based on user defined material models and user defined numerical parameters. This code is used for all the phase-field calculations reported in this work.

Considering the evolution of the phase-field from equation (2.19) and the interface shape in figure 2.12b, it is natural (and quite useful) to deduce an expression for the interface velocity. The simplest approach is to transfer the coordinate frame of (2.21) to one moving with a constant velocity,\textsuperscript{61} changing $\partial \phi / \partial t \rightarrow -v(\partial \phi / \partial x)$ in the one dimensional setting. The velocity of this front then becomes a function of the mobility, $M$, and the driving force for the transformation, which is the change in the Gibbs free energy realized by the system if the transformation proceeds. Chapter 3, and specifically section 3.2, presents the development of a new model for interface mobility, dependent on temperature and lattice parameters of the participating phases. A first approximation of $\Delta G$ for the bulk could be

$$\Delta G_{ij} = \frac{\Delta H_{ij}^{0}}{T_{ij}^{0}} (T_{ij}^{0} - T) = \Delta S_{ij}^{0} \Delta T_{ij} ,$$

(2.26)

where $\Delta H_{ij}^{0}$ and $\Delta S_{ij}^{0}$ are variations in the enthalpy and entropy, respectively and $T_{ij}^{0}$ is the equilibrium temperature. Typical thermodynamic databases have free energy functions for a wide range of composition and temperature, allowing a formulation such as

$$\Delta G_{ij} = G_{ij}^{\text{ideal}} (c_{ij}^{f}) - \sum_{t=1}^{N} c_{ij}^{t} \mu_{t}^{f} (c_{ij}^{t}) ,$$

(2.27)
where $c_i^k$ is the molar fraction of component $k$ in phase $i$, $\mu_i^k$ is the chemical potential of $k$ in phase $i$, and $G_j^\text{mol}$ is the molar Gibbs energy of phase $j$. This information can simply be read from a common Gibbs free energy diagram, such as in figure 2.14.

Figure 2.14: Thermodynamic driving force in a binary alloy for the phase-field model. The interface of phase $j$ with composition $c_j^B$ is growing in a parent phase $i$ with composition $c_i^A$.\textsuperscript{13}

Gibbs free energy diagrams will be handled in further detail in chapter 3, but the reader is also referred to the literature.\textsuperscript{14}

Another aspect of phase-field modelling that has received criticism in the past is that of nucleation. This lies in the fact that the phase field equations are designed for the motion of an existing interface and do not have any inherent capacity for the nucleation phenomenon. Simmons et al.\textsuperscript{75} have devoted some effort to incorporating the classical nucleation theory into phase-field models. In chapter 4, a new method is proposed to incorporate temperature dependent nucleation rates into both isothermal and non-isothermal models.

One of the characteristics of the phase-field model that has been prohibitive to large scale simulations is the relative numeric intensity that is required. The diffuse interface inherent in the phase-field method has a finite width, $\delta$, but is in reality in the order of a few Å. A mesh of this scale would be impractical for 2- or 3-D simulations, even with large computing power. Therefore, there is a drive to simulate with as sparse a mesh as possible while still having enough points to resolve the critical derivatives of the interface. Rodney et al.\textsuperscript{80} suggest representing the diffuse interface with typically 5 grid points to avoid another numerical effect known as ‘grid pinning’. Narrow interfaces in a discretised space have been shown to exhibit a low mobility due to numerical effects.\textsuperscript{90} Other research has shown that if the interface width is still relatively small in comparison with scale of the microstructural features of interest, some parameter modification can produce stable simulations with a sparser mesh.\textsuperscript{91} A dual-mesh strategy\textsuperscript{92} is presented in
chapter 5 which makes the microstructure modelling of a mesosopic heat affected zone more computationally feasible.
References


REFERENCES


Part II

Theory
Chapter 3

Interface Motion and Phase Transformations

3.1 Introduction

Physical descriptions of interface motion and driving forces for phase transformations are essential to the development of physically-based material models. This chapter begins with the presentation of a temperature-dependent single phase interface mobility model in section 3.2 and its application to grain boundary mobility in section 3.3. The interface mobility model is then adapted to interphase interfaces in section 3.4 and the driving force for transformation is given a physical basis. The chapter concludes with examples of diffusion in alloys, which can affect the interface motion and the overall transformation kinetics.

3.2 Interface Mobility

Before the mobility of grain boundaries can be handled, it is important to present the mechanism by which a grain boundary moves. Grain boundary motion consists of the generation of lattice sites in growing grains and the associated destruction of lattice sites in the shrinking grains, assuming that no vacancies are created. With these mechanics involved, grain interface motion can be regarded as a diffusion-like process where the interface velocity is a function of the jump distance and jump frequency, expressed as

\[ v = d \left( \Gamma_a - \Gamma_e \right) , \]

(3.1)

with \( d \) as the atomic distance and \( \Gamma_a \) and \( \Gamma_e \) the jump frequencies of atoms on either side of the interface. In a perfect bi-crystal with a fixed and known angle of misorientation across the interface, there exists an exact analytical expression for the distance between an interface position in one lattice and the nearest lattice position in the neighbouring grain. However, in real poly-crystalline materials with random grain orientations, quantifying \( d \) becomes more challenging. One approach, which inherently removes the grain orientation
dependence, involves the approximation that the average interatomic distance is related to the volume allotted to an atom in a given crystal structure, $V_A$. In an interface between two grains of the same phase, the jump distance is expressed simply as

$$d = V_A^{\frac{1}{3}}.$$  \hspace{1cm} (3.2)

For phase transformations, interface mobility must be treated with somewhat more attention than in grain growth where lattice dimensions are identical on both sides of the interface. During phase transformations, an interface separates grains with different lattices, and therefore different interatomic distances. With reference to equation 3.2, $d$ between an $\alpha$-phase and a $\beta$-phase can be reformulated as

$$d = \frac{1}{2} \left( V_\alpha^{\frac{1}{3}} + V_\beta^{\frac{1}{3}} \right),$$  \hspace{1cm} (3.3)

where $V_\alpha$ and $V_\beta$ are the atomic volumes in phases $\alpha$ and $\beta$ respectively.

In the context of interface motion in materials science, what is referred to as a driving force is actually an amount of energy per unit volume. However, expressing $[\text{J m}^{-3}]$ as $[\text{N m}^{-2}]$ presents this energy as an equivalent force per unit area, or pressure. Generally, a driving force for grain boundary migration is present if the movement leads to a reduction in the total free energy of the system$^*$. 

The driving force for the growth of a grain can be described as an energy per unit volume, or $F = -dG/dV$, where the potential energy release of one atom moving from one grain to the other is $Fd^2$, assuming $V_A = d^3$. This happens along the entire interface, as depicted in figure 3.1. The jump frequency is composed of the characteristic vibration of the lattice (Debye frequency, $\nu_D$) and the influence of the migrational/diffusional activation energy, $Q_m$, so that equation 3.1 can be rewritten as

$$v = d \nu_D \exp \left( \frac{-Q_m}{kT} \right) \left( 1 - \exp \left( \frac{-F d^3}{kT} \right) \right).$$  \hspace{1cm} (3.4)

In reality, atoms within a lattice vibrate with a spectrum of frequencies. However, next to a crystal defect (such as a grain boundary), this spectrum of vibrations is dominated by a single frequency, which is approximated by the Debye frequency in this work. For most practical purposes,$^1$ $Fd^3 \ll kT$ so that $\left( 1 - \exp \left( \frac{-F d^3}{kT} \right) \right) \approx \frac{F d^3}{kT}$, which leads to

$$v = \frac{d^3 \nu_D \exp \left( -\frac{Q_m}{kT} \right)}{kT} \cdot F = M \cdot F,$$  \hspace{1cm} (3.5)

where the marked terms make up the so-called mobility, $M$, and the expression as a whole has the units $\text{m} \cdot \text{s}^{-1}$. The relation $v = MF$ has been verified experimentally for flat grain boundaries and magnetic driving forces.$^2$ The mobility can then be expressed as having a pre-exponential component and an exponential component, given by

$$M = M_o \cdot \exp \left( -\frac{Q_m}{kT} \right) \quad \text{with} \quad M_o = \frac{d^3 \nu_D}{kT}.$$  \hspace{1cm} (3.6)

$^*$In principle, a gradient of any intensive thermodynamic property is accompanied by a driving force. The gradient can be in temperature, pressure, density of defects, or stored strain energy.
3.3 Single Phase Interfaces: Grain Boundaries

3.3.1 Grain Growth

Having explained how grain boundary motion occurs, the driving force for grain boundary motion, $F$, can be quantified. The general expression for $F$ is the sum of interface and bulk contributions, or

$$ F = \Delta E_{\text{int}} + \Delta E_{\text{blk}} . \quad (3.7) $$

In the case of grain growth, there is no difference between free energy of one grain interior and that of a neighbouring grain interior, and thus $\Delta E_{\text{blk}} \to 0$. The interface contribution stems from interface motion that can reduce interfacial area and thus reduce the interfacial energy of the system. The difference in interface energy in the system after interface motion can be expressed as $\Delta E_{\text{int}}$

Thermodynamically, a system with smaller grains has more interfacial free energy than a system of the same size with larger grains. This is due to the amount of interfacial...
Figure 3.1: Schematic representation of interface motion. Here, a net flux of atoms towards grain 2 causes it to grow and the interface moves left.
area and the associated interfacial energy per unit area, $\sigma$. This can be elucidated by considering the curved interface of a small spherical grain in a larger matrix. A change in position of the interface results in a change in the volume of the sphere, $\Delta V$, and a change in the area of the interface surrounding the sphere, $\Delta A$. The change in free energy of the system associated with the motion of the interface then becomes

$$\Delta E_{\text{int}} = -\sigma \cdot \frac{\Delta A}{\Delta V} = -\sigma \cdot \kappa,$$

where $\Delta A/\Delta V$ being expressed as the local curvature, $\kappa$. This implies that the velocity of the interface, from the perspective of the small spherical grain, is negative and the size of the sphere will decrease. From the perspective of the surrounding matrix, the velocity is positive. Figure 3.2 depicts how the influence of curvature will drive grain growth in a schematic microstructure. Growing grains with microscopically negative curvatures are often observed experimentally.\(^1\)

Figure 3.3 compares analytical calculations of grain boundary movement with numerical results from phase-field calculations using MICRESS\(^\text{®}\), which is based on the work of Steinbach et al.\(^2\) The phase-field domain is composed of a $200 \times 200$ grid, with a spacing between grid points of $0.1 \ \mu m$. A small grain with a radius of $5.0 \ \mu m$ is centred in a matrix of the same phase, as shown in figure 3.3a. During the simulation, the interface front is tracked along the shown arrow. The mobility is set to $M = 1.0 \cdot 10^{-12} \ m^4/(J \ s)^{-1}$ and the interfacial energy is prescribed as $\sigma = 0.8 \ J \ m^{-2}$, which corresponds to the typical large-angle grain boundary energy in steel. As shown in equation 3.8, the driving force for grain boundary motion is the reduction of interface energy in the system. After $10 \ s$, the radius of the small grain has been reduced by $50\%$, thereby reducing the interface energy of the system by $75\%$. The specific grain boundary energy remains constant, but the local curvature increases as the small grain is consumed, leading to an increase in the driving
force. This is evident in the non-linear evolution of the grain boundary position with time, shown in figure 3.3c. As shown, the phase-field method captures both qualitative and quantitative aspects of the analytical solution.

A further numerical consideration is highlighted in figure 3.3c, namely the choice of interface width. This is a user-defined parameter in MICRESS®. As mentioned in the introduction of the phase-field method in section 2.3.3, the interface is approximated with a continuous, differentiable function for the change of the phase-field variable for that grain, \( \phi_i \), from some maximum value inside the grain to some minimum value outside the grain. The maximum and minimum for each phase field variable is typically 1 and 0 respectively. In the numerical setting, if this transition occurs over a distance that is too small, differentiability becomes endangered and the solution could lose stability. However, overly thick interfaces can, among other problems, also lead to premature extinction of small grains, as shown by the simulation with \( \delta = 20 \) cells in figure 3.3c. The choice of interface width which resulted in a better agreement with the theoretical grain boundary position was given by \( \delta = 5 \) cells. Practical experience has shown that interface widths should be as small as possible, ideally less than one quarter of the radius, while still keeping the phase-field domain tractable for the available computer memory. Typically, \( 2.25 \cdot 10^9 \) grid points occupies 2 GB of memory, although some optimisation and simulation specifics may change this slightly.

### 3.3.2 Recrystallisation

Strain energy is introduced into a material by an arbitrary deformation process. Because of varying orientations with respect to the applied stress causing the deformation, some grains have activated slip systems aligned with the stress and allow the dislocations to form and pass through the crystal while other grains have less favourable slip systems and are more resistant to dislocation formation. The density of dislocations is related to the stored strain energy. Therefore, the varying orientations of the grains can lead to different amounts of strain energy in different grains. If, alter or during the deformation process, the atoms have sufficient thermal energy, the lattice can recover from its distortion. This leads to a reduction of the stored strain energy through annihilation and rearrangement of dislocations. Given higher thermal energy and a minimum amount of stored strain energy, another mechanism for relieving the strain energy becomes active, namely recrystallisation.

The classical treatment of recrystallization characterizes it as a process of nucleation and growth.\(^2\)\(^-\)\(^9\) The general consensus currently, however, is that recrystallization does not occur by means of classical nucleation but rather involves the transformation and growth of ‘pre-formed nuclei’ or subgrains,\(^5\)\(^-\)\(^7\) the size of which can be several micrometers. The location of a transforming subgrain is also determined by the position where the least amount of new interface will be introduced. Therefore, the most thermodynamically favorable location is a subgrain that lies next to an existing grain boundary or triple (and higher order) junction.

Values for the stored strain energy can be obtained through calorimetric experiments in which the energy necessary to heat a sample that has been cold-worked is compared to the energy necessary to heat an annealed sample.\(^6\) In the absence of calorimetric measurements, theoretical estimates using the dislocation density can be made. The dislocation density, \( \rho \), has been shown\(^8\) to be related to the material shear modulus \( G \).
Figure 3.3: A grain with an initial radius of 5 μm is placed in a matrix of the same phase. The analytical solution for grain boundary position (relative to the grain centre) is compared with numerical results from grain growth (GG) simulations using the phase-field method. The analytical calculation are based on \( v_{\text{rel}} = M(-\sigma \kappa) \) with \( M = 1.0 \times 10^{-12} \text{ m}^4 \text{s}^{-1} \) and \( \sigma = 0.8 \text{ J m}^{-2} \). Phase-field simulations used the same parameters with the additional specification of the number of cells in the interface, \( \delta \).
Burgers vector $b$, and yield stress $\sigma$, via

$$\rho = \left( \frac{2 \sigma}{G b} \right)^2.$$ \hfill (3.9)

The stored strain energy, $E_c$, is then derived as

$$E_c = \frac{1}{2} \rho G b^2.$$ \hfill (3.10)

During the simulation of recrystallization, contributions from the bulk to the driving force for interface motion (see equation (3.7)) cannot be neglected. The bulk property in question is the stored strain energy, $E_c$. Assuming recrystallization can completely release this stored strain energy, the difference in bulk free energy between a grain that has not recrystallised and a recrystallized grain can be expressed as

$$\Delta E_{\text{blk}} = E_c.$$ \hfill (3.11)

Contributions to the driving force from the interfacial energy are still active, leading to the expression for the interface velocity:

$$v_{\text{int}} = M [E_c - \sigma \cdot \kappa].$$ \hfill (3.12)

Differences in stored strain energy across a grain boundary can cause a small recrystallised grain to grow if $E_c > \sigma \kappa$, in spite of the unfavorable interface curvature.

In simulations of recrystallisation, a minimum stored strain energy is defined. A grain possessing less than the critical stored strain energy cannot host a new recrystallised sub-grain. Recrystallisation simulations are presented and discussed in chapter 6.

### 3.4 Multiple Phase Interfaces: Phase Boundaries and Thermodynamics of their Motion

#### 3.4.1 Pure Materials

For phase transformations, just as with recrystallisation, $\Delta E_{\text{blk}} \neq 0$. The bulk contribution for phase transformation stems from the difference in Gibbs free energy, $\Delta G$, between the phases considered. This expands the expression for $F$ from equation 3.7 to

$$F = -\sigma \cdot \kappa + \Delta G.$$ \hfill (3.13)

Before implementing this in an example, a brief review of the thermodynamics is required to understand the basis of $\Delta G$.

Recalling fundamental thermodynamics and combining the first and second laws, the change in the internal energy of a closed system, $\mathcal{U}$, can be described as

$$d\mathcal{U} = T \cdot dS - P dV,$$ \hfill (3.14)

where $T$ is the temperature, $S$ is the entropy, and $P$ and $V$ are the pressure and volume of the system respectively. Due to practical considerations, it is desirable to reformulate
3.4. **MULTIPLE PHASE INTERFACES**

Equation 3.14 from an expression with $S$ and $V$ as independent variables to one with $T$ and $P$. The Gibbs free energy achieves this by describing free energy in terms of the enthalpy, $H$, and entropy, and is expressed as

$$G = H - TS. \quad (3.15)$$

For a pure material having multiple phases, the Gibbs free energy can be expressed per phase. Assuming constant pressure, temperature determines which phase is stable and the transition between the stability of the two phases occurs at a single temperature. At that transition temperature, $T_\alpha$, both phases are in equilibrium, meaning that the Gibbs free energy of both phases is equal. This allows

$$G_\alpha = H_\alpha - T_\alpha S_\alpha$$

$$G_\beta = H_\beta - T_\beta S_\beta$$

$$\Delta G_{\alpha-\beta} = H_{\alpha-\beta} - T_\alpha S_{\alpha-\beta} \quad (3.16)$$

with $H_{\alpha-\beta}$ and $S_{\alpha-\beta}$ being the enthalpy and entropy of formation respectively. Since the Gibbs free energies are equal at equilibrium, $\Delta G_{\alpha-\beta} = 0$ and the entropy of formation can be expressed as

$$S_{\alpha-\beta} = \frac{H_{\alpha-\beta}}{T_\alpha}. \quad (3.17)$$

When the temperature varies from $T_\alpha$, the Gibbs free energy difference between the two phases no longer remains zero. Assuming that $H_{\alpha-\beta}$ and $S_{\alpha-\beta}$ remain relatively constant with the temperature variation,

$$\left( \frac{\partial \Delta G_{\alpha-\beta}}{\partial T} \right)_P = \left( \frac{\partial (H_{\alpha-\beta} - T_\alpha S_{\alpha-\beta})}{\partial T} \right)_P$$

$$\left( \frac{\partial \Delta G_{\alpha-\beta}}{\partial T} \right)_P = -S_{\alpha-\beta}. \quad (3.18)$$

Therefore, for temperature change resulting in an undercooling of $\Delta T$ in a pure material, the driving force for transformation is

$$\Delta G_{\alpha-\beta} = -S_{\alpha-\beta} \cdot \Delta T \quad (3.19)$$

where the convention is adopted that larger driving forces for transformation are increasingly negative. This is a fundamental principle in understanding how the chosen phase-field code translates thermal deviation from equilibrium into a driving force for transformation. It should be emphasized that the use of equilibrium transformation temperatures in the material models does not require a transformation to take place at the instant of passing through the transformation temperature. The deviation from the equilibrium temperature simply determines the driving force for transformation. Since the composition of both phases in a pure material is identical, no diffusion has to occur across the interface. The interface mobility, just as was the case for grain growth, is the controlling factor in the transformation kinetics. With the form of $F$ from equation 3.13, the local interface velocity is expressed as

$$v_{\text{int}} = M_{\alpha\beta} \left[ \Delta G_{\alpha-\beta} - \sigma_{\alpha-\beta} \kappa \right] \quad (3.20)$$

Figure 3.4a shows an example microstructure having a grain of phase $\beta$ in an $\alpha$ matrix. The grid construction is identical to that in figure 3.3, namely 200 x 200 with a 0.1 $\mu$m
spacing between grid points. In this example, $\beta$ is the high-temperature phase and $\alpha$ is the low-temperature phase. The transition temperature is 1000.5 K and the system is held isothermally at 1000.0 K. The entropy of formation, $S_{\alpha-\beta}$ is $2.5 \cdot 10^6$ J m$^{-2}$ K$^{-1}$. leading to $\Delta G_{\alpha-\beta} = 1.25 \cdot 10^5$ J m$^{-3}$. Mobility is set to $1.0 \cdot 10^{-12}$ m$^4$ (J s)$^{-1}$ and the interfacial energy is 0.8 J m$^{-2}$. After 10 seconds, as shown in figure 3.4b, the $\beta$-grain has a radius of 1 $\mu$m. The analytical solution for the interface position is shown as a solid line in figure 3.4c while the data points represent the numerical phase-field solution. For comparison, the phase-field result from figure 3.3 is included, showing the distinct effect of $\Delta G_{\alpha-\beta}$ on the interface kinetics.

### 3.4.2 Alloys

Although pure materials are important for clear examples and other highly specialised purposes, the most common materials are alloys. In alloys, the Gibbs free energy depends not only on temperature and pressure, but also on (local) composition. For this investigation, it is useful to consider the thermodynamic basis for transformations in arbitrary solutions. Similar to the pure material with two phases (see section 3.4.1), the Gibbs free energy of a single-phase, binary $A - B$ solution at a fixed $T$ and $P$ can be expressed as

$$G = x_A G_A + x_B G_B + \Delta G^M, \quad (3.21)$$

where $x_A$ and $x_B$ are the molar fractions of $A$ and $B$, the partial free energy of the pure $A$ and $B$ is $G_A$ and $G_B$ respectively, and $\Delta G^M$ is the difference between the free energy of the pure components and the free energy of the mixed solution.

Following the form of equation (3.15), the free energy of mixing is

$$\Delta G^M = \Delta H^M + T \cdot \Delta S^M. \quad (3.22)$$

#### Ideal Solutions

For an ideal solution, the process of mixing is neither endothermic nor exothermic and $H^M \to 0$. From statistical thermodynamics, the entropy of mixing is

$$\Delta S^M = k \cdot \ln \omega \quad \text{where} \quad \omega = \frac{(N_A + N_B)!}{N_A!N_B!}, \quad (3.23)$$

where $N_A$ and $N_B$ are the number of $A$ and $B$ atoms in the system and $\omega$ describes the number of realisations of the system. For one mole of solution, $N_A + N_B = N_a$ with $N_a$ is Avogadro’s number. Using Stirling’s approximation ($\ln \xi \approx \xi \ln \xi - \xi$), the entropy of mixing can be expressed as

$$\Delta S^M = k [N_a \ln N_a - x_A N_A \ln(x_A N_a) - x_B N_B \ln(x_B N_a)], \quad (3.24)$$

Since $R = k \cdot N_a$,

$$\Delta S^M = R [x_A \ln(x_A) + x_B \ln(x_B)] \quad (3.25)$$

and, for an ideal solution,

$$\Delta G^M = -RT [x_A \ln(x_A) + x_B \ln(x_B)] \quad , \quad (3.26)$$

which substituted into equation (3.21) results in

$$G = x_A G_A + x_B G_B + RT [x_A \ln(x_A) + x_B \ln(x_B)], \quad (3.27)$$
3.4. **MULTIPLE PHASE INTERFACES**

![Diagram showing phase interfaces at different times](image)

(a) $t = 0$ s.  
(b) $t = 10$ s.

(c) Evolution of grain radius with time.

**Figure 3.4:** Analytical solution for grain boundary position (relative to the grain centre) compared with numerical results from phase transformation (Trans.) simulations with the phase-field method. Analytical calculation based on $v_{\text{int}} = M(-\sigma_{K} + \Delta G_{\alpha-\beta})$ with $M_{\alpha-\beta} = 1.0 \cdot 10^{-4}$ [cm$^4$(J s)$^{-1}$], $\sigma_{\alpha-\beta} = 8.0 \cdot 10^{-5}$ [J cm$^{-2}$], and $\Delta G_{\alpha-\beta} = 0.125$ [J cm$^{-3}$]. The phase-field simulation used the same parameters. For comparison, phase-field results from grain growth simulations were included.
**Chemical Potential**  For additions of $A (dn_A)$ or $B (dn_B)$ which are small enough that the composition is negligibly changed, the free energy of the system is increased by $dG' = \mu_A \cdot dn_A$. The proportionality constant, $\mu_A$, which is also known as the chemical potential, is dependent on the composition of the host phase, so $dn_A$ must be small. If additions of $A$ and $B$ are made in proportion to the composition (i.e. $n_A' / n_B' = (n_A + dn_A) / (n_B + dn_B)$), then

$$G = \left(G_A - RT \ln(x_A)\right) x_A + \left(G_B - RT \ln(x_B)\right) x_B.$$  \hspace{1cm} (3.28)

**Real Solutions with Activity**  The enthalpy of mixing, $\Delta H^m$, becomes non-negligible when the atoms in a solution exhibit a preference for neighbouring atoms (i.e. the bond strength between $A$ and $B$ atoms is different than that of $A-A$ bonds or $B-B$ bonds). The influence of the preferential bonds on the enthalpy of mixing can be expressed by the activity, $a_i$, of a given component. The activity in binary solution is defined such that

$$a_A = \exp \left(\frac{\mu_A - G_A}{RT}\right) \quad \text{and} \quad a_B = \exp \left(\frac{\mu_B - G_B}{RT}\right).$$  \hspace{1cm} (3.29)

Graphically speaking, $a_A$ is the value which makes $-RT \ln a_A$ equal to the free energy difference indicated by the line segment $ac$ in figure 3.5. Likewise, $a_B$ makes $-RT \ln a_B$ equal to the free energy difference indicated by the line segment $bd$. This translates equation (3.28) into

$$G = x_A G_A + x_B G_B - RT \left[ x_A \ln(a_A) + x_B \ln(a_B) \right],$$  \hspace{1cm} (3.30)

where the influence of using activities $a_A$ and $a_B$ is shown in figure 3.5 by $\Delta H^m$. For an ideal, dilute solution of $B$ in $A$ where $x_B \to 0$, then the activity $a_A$ is approximately equal to the molar fraction of $A$, or $a_A / x_A \approx 1$. This is said to obey Raoult’s law. For the small amounts of $B$, it is observed that $a_B / x_B$ is approximately constant, which is said to obey Henry’s law.

The considerations to this point are important in order to understand how free energies of alloys originate. However, in a general alloy, there is a factor which has a substantial influence on the free energy of the solution, namely the size difference between $A$ atoms and $B$ atoms. The methods presented to this point will underestimate the free energy of a real solution since the strain energy caused by the size mismatch is neglected. Nevertheless, modern thermodynamic databases have tabulated experimental data for the activities as a function of composition for most alloys. Since the values for these activities are measured from real materials, all the influences of strain energy and bond strengths are implicitly incorporated. All the thermodynamic data used in this thesis makes use of these measured activities in order to calculate the Gibbs free energy curves for phases and the driving forces for transformation.

**Multiple Phases**  From the case of a single phase in a binary mixture, the step to considering two phases is quite logical. In this case, the molar fraction of $A$ in one phase, say $\alpha$, is $x_A' = 1 - x_B'$ just as the composition in the other phase, say $\beta$ is given by $x_A'' = 1 - x_B''$. For readability in the following equations and diagrams, $x_A' \equiv x'$ and
\( x^\alpha_A \equiv x^\beta \). The Gibbs free energy curves of the two phases are then given by two equations in the form of 3.27, namely

\[
G' = x'^\alpha G_A + (1-x'^\alpha)G_B - RT x'^\alpha \ln(x'^\alpha) + (1-x'^\alpha) \ln(1-x'^\alpha)
\]

\[
G^\beta = x^\beta G_A + (1-x^\beta)G_B - RT x^\beta \ln(x^\beta) + (1-x^\beta) \ln(1-x^\beta)
\]

(3.31)

Figure 3.6a shows two such curves at two temperatures. The equilibrium phase diagram based on these curves is shown in figure 3.6b. The curves for the \( \alpha \)-phase are given in red while the curves for the \( \beta \)-phase are shown in blue. The dashed lines in figure 3.6a represent the Gibbs free energy curves at temperature \( T_1 \). If a solution of composition \( x_o \) was cooled from the single \( \beta \)-phase region to \( T_1 \) and \( \alpha \) had not yet had a chance to form, the chemical potential of \( A \) in the \( \beta \)-phase would be \( \mu_A^\beta(x_o) \). This is indicated by the tangent line to the \( \beta \)-curve at the \( x_o \) composition. With the introduction of the \( A \)-rich \( \alpha \)-phase, the composition of \( \beta \) shifts to the right. The tangent to the Gibbs free energy curve of the \( \beta \)-phase shifts accordingly. When the chemical potential of \( A \) in \( \alpha \) and \( \beta \) is the same, the condition of equilibrium has been reached and the tangents to the free energy curve of \( \alpha \) and \( \beta \) are coincident. The Gibbs free energy that is released as a result of this transformation is indicated by \( \Delta G \) in figure 3.6a. As the temperature drops further to \( T_2 \), the stability of the phases changes, which is reflected by shifts in the free energy curves and depicted by the bold lines in figure 3.6a. The shift in equilibrium composition of the phases can also be seen in the equilibrium phase diagram.

To this point, the driving force resembles that described in section 3.4, with one important distinction: it is easily seen that if the solution in figure 3.6 were richer in \( B \), the stability of the \( \beta \)-phase would increase, just as the \( \alpha \)-phase would be more stable if the solution were richer in \( A \). This composition dependence of the driving force, based on the Gibbs free energy curves for each phase, is essential when modelling phase transformations in alloys. Standard diffusion equations with phase-dependent diffusion coefficients enable
the redistribution of the components during phase transformations to be modelled. The phase-field method provides an inherent coupling between the diffusion equations, the evolving driving forces for transformation, and a characteristic interface mobility.

### 3.5 Mixed-Mode Interfacial Motion

The various phases in a real, multi-phase solution have different equilibrium compositions, requiring the diffusion of alloying elements across a moving phase-interface if the system is not in equilibrium. If diffusion coefficients are different on either side of the interface, as is often the case, a complex concentration profile can develop which can significantly influence the motion of the interface. In this section, the causes for such 'mixed-mode mobility will be investigated and it will be shown how the phase-field method captures this phenomenon.

A general-purpose multi-phase phase-field code provides an ideal medium to implement the considerations from sections 3.3 and 3.4. The phase-field method allows the incorporation of a phase-dependent grain boundary energy, a phase-dependent interface mobility, and a temperature- and composition dependent driving force for transformation. In addition, as will be seen in the following examples, equating measured thermophysical properties to numerical parameters enables the phase-field method to simulate interface controlled phase transformations, diffusion controlled phase transformations, and mixed-mode phase transformations. A mixed-mode transformation is said to occur when both the reorganisation of atoms in the interface structure and the diffusion of critical species through the interface play a determining role in the progression of an interface front. Sietsma and van der Zwaag\(^2\) have presented an analytical model to predict this switch in controlling phenomenon. In their work, it was shown that the diffusion field at early stages
of transformation does not hinder the phase transformation, but rather that the interface mobility is rate limiting. At later stages in the transformation, as the diffusion field has had time to develop and the area to volume ratio of the growing phase decreases, an accumulation or depletion of the diffusing species at the interface can increase the importance of diffusion as a rate-controlling process. However, two important assumptions are made, one which influences the final stages of transformation and one which has an effect on the initial stages of transformation. In their presentation, it is assumed that the concentration at a sufficient distance from the interface remains constant. A modification would be necessary to accommodate for the case of soft impingement of diffusion fields which slow the transformation rate as the transformation nears completion. A properly constructed phase-field simulation can include the entire diffusion field (in 2- or 3-dimensions) and thus incorporates these effects. The second assumption by Sietsema and van der Zwaag is that of neglecting the interfacial energy. As seen in section 3.3 and 3.4, the effect of grain boundary energy when the area to volume ratio is large can be significant. These features are included in the following examples and due to the inherent coupling of the phase-field equations with the equations for diffusion in the phase-field method, the shift in transformation control between diffusion and interface mechanisms is automatically incorporated.

Four examples of phase-field simulations of transformation under the influence of concentration and interface mobility effects are shown in figure 3.9. Similar to the schematic phase diagram in the right of figure 3.6, the examples consider an increasing solubility of $B$ in both phases with cooling and an increasing stability of the $\alpha$-phase with cooling. The alloy has an average composition of 0.18 wt% B and is modelled as having a two-phase $\alpha + \beta$ temperature range extending from 1070 K to 805 K. The simulation commences at 1040 K with an equilibrium phase fraction of 0.44 $\beta$-phase as a single grain of homogeneous composition within an $\alpha$-matrix. At $t = 0$ s, the material immediately begins to cool at a rate of 10 K s$^{-1}$, resulting in a temperature of 890 K after 15 seconds. The slope of the $\beta : \beta + \alpha$ line (refer to figure 3.6) is 166.6 K wt%$^{-1}$ while the slope of the $\beta + \alpha : \alpha$ line is 1655 K wt%$^{-1}$. Interface mobility of the $\alpha : \beta$ interface is governed by the expression for mobility given in equation 3.6 and the parameters in table 3.1. As the temperature decreases, the mobility is reduced exponentially, according to equation (3.6).

<table>
<thead>
<tr>
<th>$d_{\lambda_{B}}$</th>
<th>$Q_{\lambda_{B}}$</th>
<th>$\nu_{\beta}$</th>
<th>$\sigma_{\alpha_{B}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.5 \times 10^{-10}$ m</td>
<td>160 kJ mol$^{-1}$</td>
<td>$6.147 \times 10^{13}$ Hz</td>
<td>0.8 J m$^{-2}$</td>
</tr>
</tbody>
</table>

Table 3.1: Interface mobility and energy parameters

The driving force for transformation is determined according to equation 3.19 with $S_{\alpha - \beta}$ as $2.0 \times 10^{5}$ J m$^{-3}$ K$^{-1}$. Note that $\Delta T$ is the difference between the current local temperature and the temperature at which the current phase fraction would be at equilibrium, and that this is dependent on the local composition. The interface mobility and the driving force for transformation progress identically for all four cases during the continuous cooling. The property which is altered is the diffusion characteristics of $B$ in the $\beta$-phase, as indicated in table 3.2. These diffusivities are plotted as a function of the inverse temperature in figure 3.7 so as to give an impression of the relative change in diffusivity among the four cases. A summary of the simulation results can be seen in figures
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3.8 and 3.9. Figure 3.9 displays concentration profiles across the phase-field domain at 2.5 second intervals through the simulation. In figure 3.8, the β-phase fraction is shown as a function of time. The phase fraction relates, of course, directly to the β grain size as analysed in the previous sections.

Table 3.2: Diffusion parameters for B. Units for \( D_0 \) and \( Q \) are [m²s⁻¹] and [kJ mol⁻¹] respectively

<table>
<thead>
<tr>
<th></th>
<th>( \beta )-phase</th>
<th>( \alpha )-phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>case 1</td>
<td>( D_0 )</td>
<td>( 2.08 \cdot 10^{-9} )</td>
</tr>
<tr>
<td></td>
<td>( Q )</td>
<td>143</td>
</tr>
<tr>
<td>case 2</td>
<td>( D_0 )</td>
<td>( 4.00 \cdot 10^{9} )</td>
</tr>
<tr>
<td></td>
<td>( Q )</td>
<td>280</td>
</tr>
<tr>
<td>case 3</td>
<td>( D_0 )</td>
<td>( 1.00 \cdot 10^{1} )</td>
</tr>
<tr>
<td></td>
<td>( Q )</td>
<td>375</td>
</tr>
<tr>
<td>case 4</td>
<td>( D_0 )</td>
<td>( 1.00 \cdot 10^{9} )</td>
</tr>
<tr>
<td></td>
<td>( Q )</td>
<td>385</td>
</tr>
</tbody>
</table>

The phase fraction as a function of cooling time is shown in figure 3.8. Case 1 is the reference case in which \( B \) diffusion in \( \beta \) has the same values as carbon in austenite. The transformation always proceeds at a higher rate in case 2 and always proceeds slower in case 3. Case 4 is the most interesting when comparing to the reference case 1. The transformation rate in case 4 is initially higher than that of case 1 and by 4 seconds (1000 K), the transformation rates are virtually identical. Further cooling reduces the transformation kinetics in case 4 to such an extent that not only the rate becomes slower than that in case 1, but the phase fraction of \( \beta \) in case 1 surpasses that in case 4 after 8 seconds.

More detailed information about the concentration profiles can be seen in figure 3.9. A noticeable accumulation of \( B \) on the \( \beta \)-side of the interface, seen in figure 3.9a, is due to the lower diffusivity of \( B \) in \( \beta \). Nevertheless, \( B \) diffuses into \( \beta \) and it can be seen that the middle of the \( \beta \)-grain also enriches in \( B \) during the transformation. In case 2, negligible build up of \( B \) can be seen from the concentration profiles in figure 3.9b. Here, the interface mobility is the rate-controlling mechanism. Case 3 is an example where the diffusivity of \( B \) in \( \beta \) is low. Figure 3.9c indicates accumulation of \( B \) on the \( \beta \)-side of the interface and negligible diffusion of \( B \) into the middle of the \( \beta \)-grain. The most interesting case is case 4. The diffusivity of \( B \) in \( \beta \) at 1040 K is higher than in case 1. Accumulation of \( B \) along the interface in the initial steps is not as high as in case 1 or case 3 and \( B \) can diffuse to the middle of the \( \beta \)-grain, as seen in the concentration profile in figure 3.9d. However, with decreasing temperature, the diffusivity of \( B \) in case 4 drops at a much higher rate than the interface mobility. The concentration increase at the interface and the negligible further increase of \( B \) in the centre of the \( \beta \)-grain is evidence of this.

This hypothetical case study has shown that a general-purpose phase-field code can capture the complex changing character of phase transformation kinetics in a physically-based approach. Diffusion controlled, interface controlled, and mixed-mode transformations can be captured in simulations which account for interfacial energy and derive the
3.5. MIXED-MODE INTERFACIAL MOTION

Figure 3.7: Temperature dependence of diffusivity in cases 1-4 presented in table 3.2. For reference, the start and end temperatures of the continuous cooling simulations are also given.

Figure 3.8: Phase-fraction as a function of time for varying behaviour of the diffusing species.
Figure 3.9: Mixed-mode mobility demonstrated with a shrinking β-particle in an α-matrix. Variation in the diffusivity of B for each case is shown in figure 3.7. Interface mobility is the same for all 4 cases.

Driving force for transformation based on local composition.
References


Chapter 4

Nucleation

4.1 Classical Nucleation Theory

The theory behind the nucleation phenomenon has undergone a long development, starting with the works by Gibbs\(^1\) and undergoing numerous refinements through the years.\(^2\) The classical nucleation theory (CNT) describes the rate at which potential nucleation sites develop into stable nuclei. In a perfect lattice, every atom represents a potential nucleation site. However, nucleation in real materials shows a strong preference for nucleation at defects in order to maximise the reduction of free energy in the system. At the moment that a material is subjected to conditions which favour the introduction of a new phase, clusters of atoms begin to form. These clusters of atoms, often called embryos, have the configuration of the new phase but have not yet reached a stable size and can collapse. This atomic traffic is governed by a diffusion-based motion, described by

\[
\beta^* = \frac{kT}{h} \exp\left(\frac{-Q_h}{kT}\right),
\]

(4.1)

where \(Q_h\) is the activation energy for diffusion in the hosting matrix and \(\beta^*\) is to be distinguished from \(\beta\) which represents a phase.

The total number of potential nucleation sites is given by \(N\). Due to local conditions influencing the development of an embryo, a size distribution is established and only a small fraction of the total potential nucleation sites host embryos of the critical size. This effect is described by the Zeldovich factor, \(z\), which is expressed as

\[
z = \sqrt{\frac{-1}{2\pi kT}} \left(\frac{\partial^2 \Delta G}{\partial \eta^2}\right)_{\eta^*},
\]

(4.2)

where the partial differential of the free energy of the embryo with respect to the number of atoms in the embryo is evaluated at the critical embryo size. This differential is very difficult to evaluate, but researchers have often used the value of 0.05 for \(z\) in the past.\(^3\)

The critical size for an embryo to become a stable nucleus is determined by several factors. Atoms joining the embryo and thus forming a more stable phase than the parent
phase reduce the free energy of the system by

\[ \Delta G_{\text{prt}} = \Delta G_{\text{t}} - \Delta G_{\text{e}}, \]

(4.3)

where \( \Delta G_{\text{t}} \) is the difference in chemical free energy of phases per unit volume and \( \Delta G_{\text{e}} \) is the introduction of any strain energy per volume due to the transformation. However, the embryo also introduces interfacial energy in the system which represents a driving force for atoms to leave the embryo. If the shape of the embryo is approximated as a sphere, then the reduction of free energy in the system due to joining the embryo and thereby forming the more stable phase is proportional to \( r^3 \), where \( r \) is the embryo radius. The increase in free energy due to the growth of the embryo, on the other hand, is a function of the embryo interfacial area and thus proportional to \( r^2 \). As seen in figure 4.1, the interfacial energy term is dominant for small embryos making them unstable until they have reached a critical size. For the schematic example in figure 4.1, both the free energy release per unit volume of transformed material, \( \Delta G_{\text{prt}} \), and the interfacial energy per unit area, \( \sigma \), have the value of unity and the radius has arbitrary length units. It is clear that a significant threshold must be overcome before an embryo reaches its critical size and becomes a stable nucleus. This threshold is the determining factor in observed instances of liquids cooled below their freezing temperature. Nevertheless, it should not be forgotten that for non-perfect, solid material, there is an important factor which reduces the threshold for nucleation. As mentioned above, nucleation at a defect also removes the free energy associated with the defect. These defects include vacancies, dislocations, and grain boundary faces, edges and corners. Nucleation at grain boundaries is most common and will be investigated more closely.

Figure 4.1: Free energy balance during the development of an embryo to a stable, growing nucleus. In this example, the free energy, \( \Delta G \), has units of joules while the radius of the embryo/nucleus, \( r \), has arbitrary units of length.
4.1. CLASSICAL NUCLEATION THEORY

Consider a spherical embryo of phase $\alpha$ forming at a planar $\beta : \beta$ grain boundary as shown in figure 4.2a. The embryo introduces $\sigma_{\alpha\beta} \cdot 4\pi r^2$ interfacial energy while removing $\sigma_{\beta\beta} \cdot \pi r^2$ in prior grain boundary energy, as shown on the right of figure 4.2a. Then the energy balance between $\Delta G_{uc}$ and the interfacial energies reads

$$\Delta G_n = -\Delta G_{uc} \cdot \frac{4}{3} \pi r^3 + \sigma_{\alpha\beta} \cdot 4\pi r^2 - \sigma_{\beta\beta} \cdot \pi r^2 ,$$

(4.4)

where the convention is that free energy release is negative. The critical embryo size is then, as illustrated in figure 4.1, the point where $\partial \Delta G_n / \partial r = 0$. Isolating for $r$ in the differential yields a critical embryo size for planar face nucleation of

$$r_f^* = \frac{4\sigma_{\alpha\beta} - \sigma_{\beta\beta}}{2 \Delta G_{uc}} .$$

(4.5)

If the assumption is made that $\sigma_{\alpha\beta} \approx \sigma_{\beta\beta} \equiv \sigma$, then the energy balance for an embryo to reach critical size is

$$\Delta G_{n(f)} = \frac{9\pi \sigma^3}{4 \Delta G_{uc}^2} = \frac{\Psi_f}{\Delta G_{uc}^2} \text{ where } \Psi_f = \frac{9\pi \sigma^3}{4} .$$

(4.6)

These considerations combine to form the CNT expression for the nucleation rate of potential face nucleation sites, $N_f$, with

$$N_f = z\beta^* N_i \exp \left( \frac{\Delta G_{n(f)}}{kT} \right)$$

(4.7)

where $N_f$ is the total number of potential face nucleation sites. The implicit temperature dependence should be treated with care as the expression is valid for isothermal nucleation at a given temperature, but does not reflect the evolution of the nucleation rate as a function of temperature during a cooling or heating transformation. This requires special attention and will be treated in following sections.

The presented case of nucleation at a planar grain boundary is but one example of three important types of grain boundary nucleation. Nucleation of a spherical embryo at a triple junction edge, as shown in figure 4.2b, removes more prior grain boundary than in planar grain boundary nucleation. This reduces the critical embryo size $t_c$

$$r_e^* = \frac{8\sigma_{\alpha\beta} - 3\sigma_{\beta\beta}}{4 \Delta G_{uc}}$$

(4.8)

which leads to

$$\Delta G_{n(e)} = \frac{125\pi \sigma^3}{96 \Delta G_{uc}^2} = \frac{\Psi_e}{\Delta G_{uc}^2} \text{ where } \Psi_e = \frac{125\pi \sigma^3}{96} .$$

(4.9)

A more energetically favourable type of grain boundary nucleation is the point where 4 (or more) grains contact, also known as a grain corner. For illustrative purposes, the contact point between 8 cubic grains, referred to here as a simple cubic corner, will be considered. This situation is depicted in figure 4.2c, with the original grain boundary removed due to the embryo shown on the right. In this case, assuming a spherical embryo, the critical radius is

$$r_{ec}^* = \frac{4\sigma_{\alpha\beta} - 3\sigma_{\beta\beta}}{2 \Delta G_{uc}}$$

(4.10)
and the energy balance at the critical embryo radius is

\[ \Delta G^\ast_{\text{sec}} = \frac{8\pi \sigma^3}{96 \Delta G^2_{\text{nc}}} = \frac{\Psi_{\text{sec}}}{\Delta G^2_{\text{nc}}} \quad \text{where} \quad \Psi_{\text{sec}} = \frac{8\pi \sigma^3}{96}. \tag{4.11} \]

This represents a significantly lower energy balance than was the case for grain boundary face or edge nucleation. However, it should be realised that the cubic geometry of the original grains shown in figure 4.2c represents a highly inefficient configuration of interfaces in space and one which is not observed in nature.

A more realistic geometry of the grains in the hosting microstructure is that of a 14-sided tetraodecahedron. For a given density of simple polygonal bodies in a volume, the tetraodecahedron shape has been shown to be the most efficient configuration of interfaces in space and is commonly used to model grains in crystalline materials. In a network of orthic tetraodecahedra, four grains contact at a corner point. In figure 4.2d showing orthic tetraodecahedron corner nucleation, the fourth grain is removed for clarity and the removed interface area due to the embryo is shown on the right. In this case,

\[ r^\ast_{\text{otec}} = \frac{8\sigma_{\alpha\beta} - \frac{1}{2} \sigma_{\beta\beta}}{4 \Delta G_{\text{nc}}} \tag{4.12} \]

and the energy balance at the critical embryo size is

\[ \Delta G^\ast_{\text{otec}} = \frac{217 \pi \sigma^3}{96 \Delta G^2_{\text{nc}}} = \frac{\Psi_{\text{otec}}}{\Delta G^2_{\text{nc}}} \quad \text{where} \quad \Psi_{\text{otec}} = \frac{81.37 \pi \sigma^3}{96}. \tag{4.13} \]

Of course, the nucleation of one type of potential nucleation site does not rule out nucleation at other types of potential nucleation sites. Corner sites may, for example, be more energetically favourable but their nucleation does not prevent edge sites from nucleating at a slower rate. Therefore, a natural adaptation of the CNT defines the total nucleation rate as the sum of nucleation rates at various defects. This is expressed as

\[ \dot{N} = \sum_i z \beta^i N_j \exp \left( \frac{\Delta G^\ast_{\text{nuc}(j)}}{kT} \right), \tag{4.14} \]

where the index \( j \) indicates the type of potential nucleation site.

The presented theory provides valuable insight into the nucleation phenomenon, but it should be noted that it is based on assumptions, some of which are being seriously questioned due to recent experimental findings. The most important assumption presented to this point is that the embryo develops as a sphere. In the bulk of a perfect crystal, the spherical geometry would be the most energetically favourable, but in the presence of defects this assumption is not necessarily valid. In various experimental work, all parameters in equation 4.14 where treated as known with the exception of the geometrical factor \( \Psi \). Using measured nucleation rates, values for \( \Psi \) where determined and were found to be orders of magnitude lower than what would be attained from equations 4.6, 4.9, and 4.13. It was found that although no geometry could have a better volume to surface area ratio than a sphere, there were possible geometries that could allow for extremely low grain boundary energies. One such proposed geometry is the ‘pillbox-with-spherical-cap’, which can have boundary energies up to 3 orders of magnitude less than common high angle grain boundaries. However, the crystallographic restriction for such low energy
4.1. CLASICAL NUCLEATION THEORY

Figure 4.2: Schematic illustrations of various classes of potential nucleation sites. Each sub-figure illustrates a spherical nucleus forming at the various potential nucleation sites on the left. On the right of each sub-figure, the portion of original interface that is removed due to nucleation is shown on the right.

boundaries \(\{111\}_\gamma // \{110\}_\alpha\) is severe and thereby reduces the density of potential nucleation sites. Table 4.1 gives an overview of the expressions for \(\Psi\) at various types of potential nucleation sites using the assumption of spherical geometry. The following column evaluates this expression with a value for \(\sigma\) of a typical high angle grain boundary energy \(\sigma = 0.75 \text{ J m}^{-2}\). Even though a spherical embryo cannot have a low energy grain boundary orientation around its entire surface, the ‘spherical-assumption’ expression for \(\Psi\) is evaluated with \(\sigma = 0.009 \text{ J m}^{-2}\), a value used for the low energy boundaries in the pillbox model.\(^{13,9}\) These values compare much better with the values for \(\Psi\) derived from the pillbox model, given in the second last column of table 4.1. The values for \(\Psi\) based on experimental measurements are shown in the last column of table 4.1.

The scientific community is still not decided on what the exact geometry of a nucleus is or what the grain-nucleus boundary energy is. However, using experimentally determined values of \(\Psi\), the relation between the nucleus geometry and boundary energy can be given a value. In the following implementation of the CNT into phase-field simulations, the
Table 4.1: Theoretical Ψ-factors for various types of potential nucleation sites based on the spherical and pillbox geometry assumption compared with values derived from experiment. For the pillbox model, the grain boundary energy was estimated for each type of boundary, leading to a range of 0.009 to 0.044 J m$^{-2}$. Ψ has the units [J$^3$ m$^{-6}$]

<table>
<thead>
<tr>
<th></th>
<th>$\Psi_j$ (sphere)</th>
<th>$\Psi_j$ (pillbox)</th>
<th>$\Psi_j$ (experimental)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$ [J m$^{-2}$]</td>
<td>-</td>
<td>0.75</td>
<td>0.009</td>
</tr>
<tr>
<td>Face</td>
<td>(216/96) $\pi\sigma^3$</td>
<td>2.98</td>
<td>5.15 $\cdot$ 10$^{-6}$</td>
</tr>
<tr>
<td>Edge</td>
<td>(125/96) $\pi\sigma^3$</td>
<td>1.73</td>
<td>2.98 $\cdot$ 10$^{-6}$</td>
</tr>
<tr>
<td>SCC</td>
<td>(8/96) $\pi\sigma^3$</td>
<td>0.11</td>
<td>1.97 $\cdot$ 10$^{-7}$</td>
</tr>
<tr>
<td>OTC</td>
<td>(81.4/96) $\pi\sigma^3$</td>
<td>1.12</td>
<td>1.94 $\cdot$ 10$^{-6}$</td>
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</tbody>
</table>

Experimentally determined Ψ values will be used. This implies a non-spherical nucleus geometry and low energy boundaries.

4.2 Simulation of Nucleation in the Phase-Field Method

The phase-field method (PFM) was designed as a method to track the motion of an existing interface. Although the PFM has shown considerable success in representing many aspects of microstructure evolution, there is no inherent provision in the phase-field equations for the phenomenon of nucleation. Nevertheless, nucleation can be introduced in a discrete manner between time increments in the numerical setting.

4.2.1 Nucleation Type Classification

Potential Nucleation Sites at Faces: The implementation of equation 4.14 into the numerical phase-field setting requires determining the number of potential face, edge, and corner sites. The number of potential sites at grain faces in a given volume was estimated by Cahn$^{10}$ as $N_f = 3.35/(d_h \cdot a^2) \cdot V$, where $d_h$ is the diameter of the grains in the hosting microstructure, $a$ is the average atomic spacing of the hosting and nucleating phase, and $V$ is the volume of the sample. However, this relation assumes that all of the atoms in all of the interfaces are potential sites. More recent experimental work$^{3, 7, 8}$ suggests the formation of low energy boundaries and the accompanying restriction of coherency at the boundaries, leading to a significantly lower number of potential nucleation sites. It is proposed here that this lower density can be approximated by 1 potential site per grain face. Using the tetrakaidecahedron as the typical grain geometry and approximating its volume as that of a sphere results in

$$N_f^{3D} = \frac{14}{2} \cdot \frac{V}{\frac{4}{3} \pi r_h^3}$$

\hspace{1cm} (4.15)

where $r_h$ is the average radius of the hosting phase grain and each of the 14 faces of the tetrakaidecahedron is shared between exactly 2 grains. Considering a 2D simulation of
the microstructure as a cutting plane through a 3D volume, the number of potential face sites can be estimated as

\[ N_f^{2D} = \frac{14}{2} \frac{1}{2} \frac{A}{\pi r_i^2} \]  

(4.16)

where \( A \) is the area of the simulation and it is estimated that the cutting plane intersects half of the 14 faces. Another, more tedious method of determining \( N_f^{2D} \) is the explicit counting of facial interfaces in the simulated microstructure. In 3D, this can be accomplished with repetitive sectioning of the microstructure, as shown in figure 4.3. In 2D, facial interfaces are recognized as line segments.

![Entire 3-D microstructure](image1)
![Internal view of 3-D microstructure](image2)

Figure 4.3: Simulation of 3-dimensional microstructure. Grain boundaries are represented as solid, light-coloured material while the bulk material is shown as a translucent, dark material.

The phase-field code employed here distinguishes grid points belonging to a facial interface from higher order junctions as the grid points which have exactly two phase-field variables greater than zero. If the nucleation routine is instructed to nucleate a potential face site, a search is performed through the valid grid points and the most thermodynamically favourable, considering both temperature and composition, is switched to the nucleating phase. If only the most favourable grid point is nucleated (i.e. one nucleation per search), then the time between searches for potential face nucleation sites is derived from equation 4.7 as

\[ \Delta t_{n(f)} = (N_f)^{-1} = \left[ z/\beta^* N_f \exp \left( \frac{\Delta G_{n(f)}^*}{kT} \right) \right]^{-1} \]  

(4.17)

where it should be noted that the implied temperature dependence will be treated in section 4.2.2.
**Potential Nucleation Sites at Edges**  The number of potential edge nucleation sites in a microstructure of tetrakaidecahedra can be approximated as

\[ N_{e}^{3D} = \frac{36}{3} \frac{V}{\frac{4}{3} \pi r_{h}^{3}} \]  

(4.18)

where each of the 36 edges of the tetrakaidecahedron are shared among an average of 3 neighbouring grains. Edges cannot be distinguished from corners in 2D as both would appear as vertices of the polygonal grains. However, since the probability of a cutting plane intersecting a corner point is much smaller than the probability of intersecting an edge, the number of vertices in a 2D simulation can be approximated as the number of edges\(^*\). Therefore, the number of edges in the plane of simulation can be approximated as

\[ N_{e}^{2D} = \frac{14}{2} \frac{1}{3} \frac{A}{\pi r_{h}^{3}} \]  

(4.19)

where, just as with the expression for grain faces in 2D, intersecting half of the 14 faces leads to a polygon of 7 vertices, each shared on average among 3 grains. Grain edges can also be manually counted. In 3D simulations, this involves multiple sectioning of a simulated volume. In 2D, all higher order junctions can be counted as edges. The expression for the time between calls to the nucleation routine for potential edge sites follows the form of equation 4.17, replacing \( N_{i} \) with \( N_{e} \) and \( \Delta G^{i}_{\text{nl}} \) with \( \Delta G^{i}_{\text{nl,e}} \). The nucleation routine is then instructed to search for grid points with more than 2 phase-field variables greater than zero. The most thermodynamically favourable location hosts the nucleation.

**Potential Nucleation Sites at Corners**  The number of potential nucleation sites at grain corners can be approximated by assuming that each of the 24 corners of a tetrakaidecahedron is shared on average among 4 grains, leading to

\[ N_{c}^{3D} = 24 \frac{V}{\frac{4}{3} \pi r_{h}^{3}} \]  

(4.20)

In 2D, as mentioned earlier, corners have a low probability of being intersected by the plane of simulation. However, if a corner is sufficiently close to the plane, nucleation of that corner will have an influence in the transformation kinetics and final grain density observed in the plane. Analysing 20 cutting planes of a 3D microstructure such as the one shown in figure 4.3 revealed that an average of 10% of the vertices in the plane had a grain corner within ±1 μm. This leads to the number of grain corners in a 2D simulation being approximated as

\[ N_{c}^{2D} = \frac{14}{2} \frac{1}{4} \frac{1}{10} \frac{A}{\pi r_{h}^{3}} \]  

(4.21)

where one tenth of the 7 vertices per grain are considered as having grain corners within 1 μm of the simulation plane and being shared among 4 grains. Again, explicit manual counting of corners in 3D can be done by multiple sectioning of a simulated microstructure.

\*Nevertheless, the number of corners **sufficiently close** to the plane of simulation which will contribute to the transformation in the plane is not negligible and will be discussed following the discussion on grain edges.
In 2D, 10% of the counted higher order junctions can be assumed to be sufficiently close to actual corners. The time between calls to the nucleation routine for grain corners follows equation 4.17, where \( N_t \) is replaced by \( N_c \) and \( \Delta G_{n(t)}^* \) by \( \Delta G_{n(c)}^* \). The nucleation routine also does not explicitly differentiate between edge and corner nucleation sites. However, if the densities of the edge and corner sites are uniquely defined, the respective potential sites will be sought with their own characteristic frequency. Whether a particular higher order junction is nucleated while the nucleation routine was searching for an edge or a corner is irrelevant.

### 4.2.2 Temperature Dependent Nucleation Rate

All heat treatments are, in the most strict sense, non-isothermal. If the overwhelming majority of the final microstructure is produced at a single temperature, then the isothermal rates presented in section 4.2.1 are valid. However, for most heat treatments, the final microstructure is influenced to a significant degree during the heating and cooling, and welded microstructures are no exception. This requires adapting the nucleation procedure from sub-section 4.2.1 to a non-isothermal setting.

In equation (4.14), \( z, \beta^r \) and \( \Delta G_{\nu c} \) are functions of temperature. In this and other works,\(^2, 3, 7, 8, 9\) \( z \) is approximated as 0.05 and held constant. \( \beta^r \) and \( \Delta G_{\nu c} \), however, are strongly temperature dependent. For transformation upon heating, such as the \( \alpha \rightarrow \gamma \) transformation in steels or the \( \alpha \rightarrow \beta \) transformation in the hypothetical system in figure 3.6, both \( \beta^r \) and \( \Delta G_{\nu c} \) increase with temperature, leading to a monotonic increase in \( \dot{N} \). Since the current phase-field code only nucleates a given class of nucleus with a constant nucleation rate, a logical first approximation is to discretise the entire nucleation temperature range into smaller, quasi-isothermal steps, or classes, as shown in figure 4.4. In each temperature range, a unique nucleation rate for corner, edge and face sites can be prescribed.

![Nucleation rate vs. temperature](image)

**Figure 4.4:** Schematic representation of the nucleation rate upon heating as a function of temperature and the accompanying discretisation

However, when modelling a material that undergoes temperature changes which are rapid compared to the current nucleation rate, a flaw in this method is realised. As the material enters a valid nucleation temperature range, the nucleation routine is instructed
to wait for \(1/\bar{N}\) s before placing a nucleus at the most favourable position. If the material leaves that temperature range before \(1/\bar{N}\) s elapse, no nucleus is set. If the material continues to change temperature at a sufficient rate, a situation can develop where the simulated material has gone through the entire nucleation temperature range without hosting a single nucleus. An improvement on this approach involves a careful discretisation of the nucleation rate as well as the temperature range, shown in figure 4.5.

![Diagram showing nucleation rates upon heating and cooling](image)

**Figure 4.5:** Schematic representation of nucleation rates upon heating and cooling. Transformation in parentheses refers to the hypothetical system presented in figure 3.6

Consider the case of nucleation upon heating, as illustrated in figure 4.5a. In the modified discretisation, the temperature range is prescribed and initially divided into a given number of temperature steps. The average temperature of the first temperature step, say \(T_1\), \(\bar{N}(T_1)\) is calculated. This is directly followed by a loop through all the remaining temperature steps to search for a \(N(T_i) \leq \bar{N}(T_1)\). If no lower nucleation rate is encountered, \(\bar{N}(T_1)\) is valid to the end of the nucleation temperature range. At the following temperature, \(T_2\), \(\Delta N(T_2) = \bar{N}(T_2) - \bar{N}(T_1)\) is calculated and a lower nucleation rate is sought. For a monotonically increasing nucleation rate, the search will always end at the upper limit of the nucleation temperature range.

However, for the reverse transformation upon cooling, the driving force for transformation increases with decreasing temperature, but the atomic mobility (and thus \(\beta^*\)) decreases with decreasing temperature. This non-monotonic progression of \(\bar{N}(T)\) requires special attention as well\(^1\). Therefore, before searching for \(N(T_i) \leq \bar{N}(T_1)\), it must be guaranteed that for the immediately following temperature \(\bar{N}(T_i) > \bar{N}(T_1)\). If this is not the case, then the peak nucleation rate has been found, namely \(\bar{N}_{\text{max}}(T_i)\). Since the temperature immediately following \(T_i\) would produce a lower nucleation rate, the duration of this incremental nucleation rate would be negligible and is thus discarded. Also, if a \(\bar{N}_{\text{max}}(T_i)\) is confirmed, further calculation of the nucleation temperature range is unnec-

\(^1\)For clarity, it should be mentioned that temperature searches on heating are conducted for increasing temperature while temperature searches for cooling are conducted for decreasing temperature.


4.2. SIMULATION OF NUCLEATION IN THE PHASE-FIELD METHOD

The process and thus aborted. This action is allowed as long as the temperature dependence of the nucleation rate only has one global maximum in the considered temperature range.

4.2.3 Other Considerations

An important component to completing the description of temperature dependent nucleation rates is the variance of the driving force for nucleation with temperature, or $\Delta G_{\nu\tau}(T)$. At this point, it should be pointed out that the $\Delta G_{\nu\tau}$ referred to in the remainder of this chapter is the driving force which helps determine the nucleation rate via $\Delta G_{n(i)} = \Psi/(\Delta G_{\nu\tau})$. The driving force for growth is determined from the phase diagrams, as explained in chapter 3. In addition, many alloys have phases that exhibit significantly different solubility for the various components. This implies that the driving force is also composition dependent, or $\Delta G_{\nu\tau}(c)$. With the use of thermodynamic databases, a single function can be fit to the free energy in composition and temperature space. However, since the evolution of composition in the hosting phase is not directly a function of temperature, but more a result of transformation kinetics and the diffusivity of the particular species, the change in $\Delta G_{\nu\tau}(c,T)$ cannot be determined \textit{a priori} for an arbitrary thermal cycle. In the current phase-field code, the nucleation routine does not have access to the composition, although minimum, maximum, and average concentrations are a standard output. The solution at this point is to halt the calculation at regular intervals during the transformation, acquire the composition, and re-calculate $\Delta G_{\nu\tau}(c,T)$. At this point, the average composition is used in the re-calculation, but the more accurate approach would be to take the local composition of any grid point that becomes a candidate for nucleation.

Two aspects of $N_j$ also require further commentary. In designing a scheme for the simulation of nucleation under arbitrary thermal conditions, it is essential that the maximum of each type of nuclei, $N_i$, can hypothetically nucleate in each nucleation temperature range (see figure 4.5). However, during a thermal process with temperatures spanning multiple temperature ranges, the maximum number of nuclei should not be exceeded. To this end, a global counter is used to track the number of each type of nucleus that have nucleated. Should $N_j$ be reached, no further nucleation of that type will be permitted.

The second aspect of $N_j$ is that it represents the current total number of potential type-$j$ nucleation sites. Before nucleation has started, all potential nucleation sites are available. However, as nucleation proceeds, the number of potential nucleation sites still available has reduced by the number of nuclei that have been set. This can be expressed as

$$N_j = N_j^0 - N_j^*$$

where $N_j^*$ is the number of nuclei of type-$j$ that have already nucleated. Currently, the implemented phase-field code cannot communicate this change in $N_j$ to the nucleation routine during a simulation, although each nucleation event is recorded in standard output. The solution to this is, as with determining $\Delta G_{\nu\tau}(c,T)$, halting the simulation at regular intervals, adjusting each $N_j$ according to equation 4.22, recalculating $N_j$, and continuing the simulation for the following interval.
Table 4.2: Composition of C35 [wt. %].

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Mo</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.364</td>
<td>0.656</td>
<td>0.305</td>
<td>0.177</td>
<td>0.016</td>
<td>0.014</td>
<td>0.021</td>
<td>0.092</td>
<td>0.226</td>
</tr>
</tbody>
</table>

4.3 Implementation with Experimental Validation

Detailed synchrotron measurements were performed by Offerman et al.\textsuperscript{11} on annealed, fully austenitic steel samples which were cooled at a continuous cooling rate of 5 K per minute. In their work, total nuclei, nucleation rates, and phase fractions were measured. The composition of the particular alloy studied, C35, is given in table 4.2. The implementation of the presented nucleation theory into phase-field modelling of ferrite nucleation and growth is presented in this section, along with an accompanying comparison of the simulation results with the experimental findings.

4.3.1 Model Construction

For the construction of the material model for C35, thermodynamic databases were used to derive an expression for the driving force for ferrite nucleation as a function of temperature and composition. The driving force for the transformation to ferrite in austenite was calculated with MTDATA\textsuperscript{®} and found to have a quadratic dependence on temperature, \( T \), and linearly with carbon concentration within the considered compositional range (0.364 wt% < \( c(C) \) < 0.80 wt% which is equivalent to 1.67 at% < \( c(C) \) < 3.60 at%).

\[
\Delta G_{\text{mc}}(c, T) = \left[ 7.09 \cdot 10^{-2} T^2 - 1.48 \cdot 10^2 T + 8.76 \cdot 10^1 \right] c(C) + \\
\left[ -1.37 \cdot 10^{-2} T^2 + 3.06 \cdot 10^1 T + 1.72 \cdot 10^4 \right],
\]

(4.23)

where \( c(C) \) is expressed as an atomic fraction and \( \Delta G_{\text{mc}} \) is expressed in J mol\(^{-1}\). This dependence is based on the thermodynamic data, represented in figure 4.6a.

4.3.2 Results

Four simulations are presented. The first neglects CNI altogether and assumes site saturation (i.e. all nucleation simultaneously). The second simulation employs the CNI with \( \Delta G_{\text{mc}} \) only a function of temperature. The third simulation includes temperature and composition effects in \( \Delta G_{\text{mc}} \). The fourth simulation uses \( \Delta G_{\text{mc}}(c, T) \) as well as an updated \( N_i \).

Simulations start with the material at a temperature of 1045 K and immediately begin cooling at 5 K per minute. The site saturation simulation is assumed to require an undercooling of 10 K and thus hosts nucleation after 180 s. All CNI simulations enter the first nucleation temperature range after 60 s. However, due to the low nucleation rates at small undercoolings, the first nuclei appear somewhat later.

MTDATA\textsuperscript{®} was also used to construct a bi-linear equilibrium phase diagram for the derivation of composition- and temperature-dependent driving forces for transformation, as explained in chapter 3. The maximum temperature range for nucleation was taken from the largest temperature range in the two-phase region of the phase diagram (1040 -
4.3. IMPLEMENTATION WITH EXPERIMENTAL VALIDATION

Figure 4.6: In figure 4.6a, the driving force for ferrite formation in austenite as a function of temperature and carbon concentration, based on the thermodynamic databases of MTDATA®. In figure 4.6b, a schematic representation of the implemented bi-linear phase diagram. The pivot temperature and composition was 1010 K and 0.44 wt% carbon respectively. The high temperature slope was 375 K (wt%)_1 while the low temperature slope was 180 K (wt%)_1.

<table>
<thead>
<tr>
<th>Table 4.3: Nucleation parameters for C35</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Psi_f$ [J^3 m^{-6}]</td>
</tr>
<tr>
<td>$N_j$ [m^{-3}]</td>
</tr>
</tbody>
</table>

960 K), while the frequency for searching for favourable corner, edge and face nucleation points was determined by thermophysical material properties from the literature, as reviewed in table 4.3, and equation (4.14). The value for the activation energy for atomic motion in the hosting phase, $Q_h = 284$ kJ mol$^{-1}$, was taken from the literature.

Figure 4.7 displays the measured and the various simulation results of ferrite phase fraction as a function of time. The experimental temperature, which was also prescribed in the simulations, is plotted against the right axis. Most of the simulation results coincide with each other, but the simulation employing site saturation of the ferrite nuclei exhibits higher initial transformation kinetics.

Figure 4.8a shows experimental ferrite nucleation density compared with various simulations of ferrite nucleation density during continuous cooling. In this figure, the simulation governed by the site saturation assumption (i.e. all nuclei are set at the instant the critical temperature is reached) can be seen to significantly overestimate the experimentally determined nucleation density. The simulation ending in the second highest nucleation density is the one assuming only temperature influences on $\Delta G_{\text{ns}}$ (i.e. neglecting carbon enrichment of the austenite) and assuming a constant $N_j$. The final two
sets of simulations are difficult to distinguish from the experimental results at the scale of figure 4.8a and are shown again in figure 4.8b. Figure 4.8b shows a magnification of figure 4.8a, comparing the experimental nucleation density with results from simulations in which the influence of concentration in the retained austenite was taken into account. The simulation predicting the higher final nucleation density considered $N_f$ as a constant throughout the simulation. The simulation predicting a lower nucleation density subtracted the nucleated ferrite from the original number of potential sites. Figure 4.8c displays the number of ferrite grains at any given time during the transformation. Due to grain growth and agglomeration, some ferrite grains were consumed. Other small ferrite grains, shortly after nucleation reached a meta-stable state due to the carbon enrichment of the surrounding austenite and were subsequently removed. The number of ferrite grains in the site saturation simulation is plotted against the right axis.

It is clear from the results in figure 4.8 that the assumption of site saturation severely overestimates (by a factor of 15) the initial and final ferrite nucleus densities. This alters the transformation kinetics and will lead to simulated microstructures that vary significantly from the experimental microstructure, both in grain size and distribution. Considering figure 4.8a, the influence of temperature in the $\Delta G_{pc}(T)$-simulation can be seen in the initial increase in nucleation rate followed by the decrease in diffusivity, leading to a noticeable decrease in the nucleation rate at approximately 800 s (980 K). However, this simulation overestimates the ferrite nucleus density by a factor of 7. The result from the simulation considering both temperature and composition in $\Delta G_{pc}$ (but holding $N_f$ constant) begins to distinguish itself from the simulation disregarding composition once

Figure 4.7: Ferrite phase fraction as a function of time. Experimental results are indicated with data points. Only the simulation assuming site saturation deviates significantly from experimental findings in the early stages of transformation. Simulations used the experimental temperature data, read off of the right-hand scale, as boundary conditions.
the ferrite fraction reaches 0.10 ($t = 375$ s). At this point, the carbon enrichment of the remaining austenite begins to decrease the driving force for the transformation to ferrite. With these settings, the simulation overestimates the ferrite nucleus density by 42%. The final simulation considers $\Delta G_{\text{int}}(c, T)$ and $N_j = N_j^* - N_j^*$. The continuous reduction in $N_j$ during the simulation leads to a lower nucleation rate and a final nucleus density which is 17% larger than the experimental findings.

In all three cases which employed some form of the CNT (i.e. not including the site saturation simulation), the nucleus density was underestimated during the initial stages of transformation. This is attributed to the assumption of a homogeneous distribution of all components in the starting austenite microstructure. Electron Probe Micro Analysis (EPMA) scans of the actual material show, however, that significant banding of Mn is present. Due to the low diffusivity of Mn, this banding is not expected to be dissolved during the annealing heat treatment prior to continuous cooling. Considering the observed banding, the $\text{A}_3$-temperature in Mn-poor regions can be as much as 10 K higher than in Mn-rich regions. This leads to accelerated nucleation and growth of ferrite in the Mn-poor regions compared to the phase-field models employing the CNT and the assumption of a homogeneous Mn distribution. After the Mn-poor regions are transformed, the austenite still available to host ferrite nucleation (Mn-rich) possesses a lower than average driving force for ferrite nucleation. This manifests itself in the nucleation rates observed being lower than those predicted by the CNT in the phase-field simulations.

It is interesting to note that although the three CNT simulations produced different nucleation rates (see figure 4.8a), the number of grains remaining in the final microstructure were closer to each other, as shown in figure 4.8c. The finite nucleation rates of all three CNT cases are close enough through the initial stages of the transformation that they all reach 10% ferrite at approximately the same moment. After this point, the two simulations employing $\Delta G_{\text{int}}(c, T)$ indicate that the carbon enrichment of the remaining austenite begins to play a role in the driving force for nucleation. However, regardless of the expression for $\Delta G_{\text{int}}$, the driving force for growth (derived from the phase diagrams) is composition dependent in all cases. As can be seen in figure 4.8c, after 400 s (or a ferrite fraction of 0.15) carbon enrichment of the austenite matrix has progressed to the point that the reduced driving force for growth and the large curvature term for very small ferrite grains offset each other and lead to a stagnation of the new ferrite grains. The current phase-field code can detect such meta-stable grains and remove them. With this feature, all three CNT simulations result in comparable final ferrite grain densities.

Development of these presented nucleation routines is a part of ongoing research. In part III of this thesis, the work presented in each chapter is based on the nucleation routine at increasing levels of maturity. Although nucleation routines are used in the study of recrystallisation in chapter 6, the mechanisms involved in the formation of recrystallised grains are fundamentally different from those described in the CNT for phase transformations. These nucleation routines should therefore not be directly compared with the routines presented in this chapter. The nucleation routines developed in chapter 7 for austenite and ferrite nucleation are the predecessors to the routines presented in this chapter. Concentration effects are neglected and a constant nucleation rate is defined for both austenite and ferrite. Chapter 8 presents the nucleation routines in their final state, but with some simplifications. The influence of carbon concentration is averaged and the simulations were not interrupted to update $N_j$. 
Figure 4.8: Various simulations of ferrite nucleation during continuous cooling at 5 K min$^{-1}$ are compared with experimental data in figures 4.8a and 4.8b. The simulated number of concurrently existing ferrite grains is shown in figure 4.8c.
References


Chapter 5

Multi-Scale Modelling

5.1 Introduction

The underlying motivation for numerical modelling is to break a complex evolving problem into many smaller problems which are solvable with simple mathematical techniques. This discretisation can be done temporally by dividing the problem into smaller time steps and it can be done spatially by dividing the calculated domain into smaller regions or elements. If the problem evolves temporally, a sufficiently small time step must be chosen in order to resolve the temporal variation. When constructing a numerical model of a spatially non-homogeneous problem, the necessary element density is related to the spatial gradients of the state being modelled. These states can include temperature, stress, or strain. The total calculation time for a given number of simulation steps is proportional to the number of elements. Elements with first-order (linear) interpolation functions can only exhibit a linear gradient of the simulated state across the element. A sufficiently fine mesh can approximate higher-order state gradients at the cost of computation time. Higher-order elements calculate a quadratic or higher-order evolution of the simulated property across the element, but are computationally more expensive than first-order elements. Localised refinement of a low-order element set in the regions of interest is an effective method to reduce overall computational costs while retaining the necessary level of detail where property gradients are high.

In spite of local mesh refinement, another challenge in developing a numerical model can arise when multiple properties are required as part of the simulation results. Properties can evolve over a wide range of time- and length-scales and standard numerical modelling requires temporal and spatial discretisation to be able to resolve the smallest variation of interest. Modelling the microstructure evolution due to a welding thermal cycle is just such a problem. Representation of the thermal profile requires a spatial resolution on the order of $10^{-3} - 10^{-4}$ m while modelling the progress of a moving grain boundary requires a resolution of $10^{-9} - 10^{-4}$ m and diffusion can require resolution from $10^{-9} - 10^{-4}$ m. The enormous computational cost associated with modelling a welded workpiece of centimeters or larger with nanometer-sized elements can be avoided with multi-scaling strategies.

A strategy is presented in section 5.2 for the modelling of an evolving microstructure using a fine sub-mesh nestled within a coarse super-mesh for the calculation of the thermal
profile. This will be referred to as the dual-mesh strategy. In section 5.3, a presentation is given of an approach to incorporate the evolving microstructure as input for the material description in a thermal-mechanical simulation, namely the twin-element approach.

5.2 A Dual-Mesh Strategy

Modelling the heat affected zone microstructure of a weld bridges many length and time scales, and requires more than intelligent meshing schemes to make simulations feasible. This section describes the dual-mesh strategy, a multi-scaled modelling method designed to make microstructure modelling in a macroscopic heat affected zone more tractable. In this method, a fine microstructure sub-mesh resides in each element of a coarse thermal super-mesh, as shown in figure 5.1. The fine sub-mesh defines a small domain at which microstructure characteristics and evolution are calculated. These domains should be as small as possible to reduce computational costs; however they must be large enough to contain the characteristic length of the entity to be described. In modelling grain growth, this length would be of the same order of magnitude as the average grain diameter. In modelling phase transformations, a length on the order of the diffusion length of the fastest diffusing element would be more fitting. The thermal mesh only needs to be able to resolve the thermal profile.

The dual-mesh strategy is designed to function as follows. The thermal field is calculated on a standard, 3-D finite element (FE) mesh. Temperature and temperature gradient information in each element is then supplied to the sub-mesh residing in the element. A multi-phase field method is implemented at the sub-mesh level and uses the calculated thermal field as a prescribed boundary condition. The idea of a coarse thermal mesh to drive calculations of a finer mesh was also utilized in independent research by Ichikawa et al. A salient difference with respect to the current strategy is that Ichikawa and coworkers meshed the entire body with a fine mesh, rather than with small, discrete sub-mesh domains.

Although local thermal gradients can be quite large in welding simulations ($10^4$ to $10^5$ K m$^{-1}$), they are less significant within a microstructure domain due to its dimensions. For example, a thermal gradient in the HAZ of $10^5$ K m$^{-1}$ translates into a temperature difference of 10 K across a microstructure domain of 100 μm in length. Therefore, if the thermal gradient is less than $10^5$ K m$^{-1}$, it can be neglected in the microstructure calculations. If the thermal gradient is larger than $10^5$ K m$^{-1}$, a linearisation of the temperature gradient across the microstructure domain is sufficient as long as the domain does not extend too far.

Distances separating phase-field domains are dependent on the thermophysical properties of components and phases in the modelled alloy. Diffusion of components in the alloy plays a large role in this criterion. Unlike most discretisation methods where refining the mesh leads to convergence toward a solution, placing phase-field domains too close to each other must be handled with care. As presented here, the dual-mesh strategy sets either periodic or symmetry boundary conditions on the phase-field domains. If the distance of separation between phase-field domains is greater than a certain minimum, it is assumed that the boundaries of the phase-field domains are independent of each other.

The assumption of independent phase-field domains provides enormous computational savings, but it must be guaranteed that a component could not diffuse from one phase-
field domain to its neighbouring domain during the simulation. This would in effect lead to concentration fluxes that are not accounted for in the boundary conditions. In other words, the minimum separation distance should guarantee that soft impingement of the neighbouring concentration fields does not occur, as illustrated schematically in figure 5.2. For prolonged heat treatments, this condition could present challenges, but for the time frames considered in welding, the condition is usually easily satisfied.

An example which can clarify these thoughts is the heating of a fully austenitised microstructure with a carbon concentration inhomogeneity. Such a situation would arise after the austenitisation of a pearlite colony in a ferrite matrix. Carbon is one of the lastest diffusing species and thereby represents a worst case scenario. In this example, a circular region (with a diameter of 15 \mu m) having a carbon concentration of 0.8 wt\% carbon represents the originally present pearlite colony. The rest of the phase-field domain has a carbon concentration of 0.01 wt\% carbon. The evolution of the carbon concentration field as a response to three representative thermal cycles is simulated. If a neighbouring phase-field domain had a similar microstructure, then the schematic representation from figure 5.2 is replicated and a sufficient separation distance must be determined.

The first thermal cycle, indicated in figure 5.3a with (1), imitates the temperature history experienced by a material point approximately 150 \mu m from the fusion zone of a weld, where the welding speed is approximately 6 mm s\(^{-1}\). The resulting evolution in the concentration profile over a line extending 75 \mu m from the centre of the carbon rich region is shown in figure 5.3b. Once the temperature has dropped below 1000 K, the concentration profile remains unchanged. Since the final carbon concentration profile at 75 \mu m has not increased, soft impingement will not occur with a neighbouring diffusion field if the separation distance is at least 150 \mu m (twice 75 \mu m, as shown in figure 5.2).

The second thermal cycle resembles the temperature history of a material point 150 \mu m from the fusion zone of a weld, where the welding speed is approximately 2 mm s\(^{-1}\). Due to the longer period of time at elevated temperatures, the second thermal cycle presents
a case where a greater minimum separation distance will be required. As seen in figure 5.3c, the carbon concentration at a distance of 75 μm from the centre of the carbon rich region has increased during the thermal cycle. The separation distance between phase-field domains when simulating this process must therefore be larger than 150 μm.

Finally, a third thermal cycle reflects an isothermal hold at 1200 K. The peak temperatures in the isothermal hold are lower, but due to the extended process times, a minimum separation distance great than 75 μm is also required. As seen in figure 5.3d, soft impingement of the diffusion fields from neighbouring phase-field domains would occur after 20 s.

As presented, the dual-mesh strategy allows a one-way flow of thermal data, namely from the coarse finite element mesh to the phase-field domains. Two important considerations justify this one-way traffic of thermal information. The first consideration involves the latent heat of transformation. Although latent heat is evolved locally at the phase front of the transformation, it is released/absorbed continuously during transformation and the total amount of latent heat is a function of the moles of material transformed. If the start and end temperature of the transformation are known, then the release/absorption of latent heat can be evenly spread over the transformation temperature range so that the total energy release/absorption per mole of transformed material is equal to the latent heat of transformation. Performing this energy release/absorption locally at each finite element as the local temperature passes through the transformation temperature range allows the latent heat of transformation to be accounted for at the meso-scale, before the explicit calculation of the microstructure. The largest assumption at this stage is that the start and end transformation temperatures are known \textit{a priori}, i.e. the transformation temperature range given by the equilibrium phase diagram for the material in question. The high heating and cooling rates associated with welding can cause measurable super-heating and super-cooling, which refers to the deviation from equilibrium transformation temperatures and the transformation temperature that is experimentally observed. However, experimental work in chapter 8 has shown that for heating rates of 15 Ks\(^{-1}\), super-heating was approximately 30 K and this is considered to be of the same order of magnitude of
5.2. A DUAL-MESH STRATEGY

Figure 5.3: Three representative thermal histories are shown in figure 5.3a. The evolution of the carbon concentration for each thermal history is shown in figures 5.3b-d. Due to the short period at high temperatures, thermal cycle (1) results in a final concentration profile (there is no change in the concentration profile after 3 s) that does not lead to soft impingement at the edge of the 75 µm domain considered. Thermal cycle (2) reaches the same peak temperature as (1), but due to the prolonged times at elevated temperatures, soft impingement could occur at the boundary of the considered domain by the time the material cools to below 1000 K. Thermal cycle (3) produces a concentration profile which could lead to soft impingement after approximately 20 s.
the error in the simulated temperature profiles themselves. Secondly, the even spreading of latent heat over the transformation temperature range implies a linear rate of transformation as opposed to the commonly observed sigmoidal transformation kinetics. This effect is also regarded as negligible when considering that the release/absorption of energy from neighbouring elements occurs at individual rates (dependent on the rate at which the local element temperature passes through the transformation temperature range), which soon masks any clean sigmoidal energy release/absorption.

The second consideration justifying the thermal data flow from the coarse finite element mesh to the phase-field domains relates to the other possible heat source resulting from microstructure evolution, namely heat dissipation due to plastic deformation. Both thermal strains and displacive phase transformations can cause plastic deformation. However, the plastic deformation from thermal straining is assumed to occur at a low rate and the plastic deformation due to phase transformation is considered to be small enough that there would be negligible influence on the temperature field.

5.3 Twin-Element Strategy

An important application of the dual-mesh strategy and the theoretical microstructure models behind them is the calculation of mechanical properties of the welded material. Spatially resolved simulated transformation kinetics, microstructure morphology and phase fractions all play a role in determining the material properties and are data which are readily available after application of the dual-mesh strategy. In this subsection, a simple method is proposed by which the effects of the evolving microstructure can be calculated in a thermal-mechanical simulation.

Consider a material which is completely of the $\alpha$-phase. Mechanical properties, such as the temperature- and plastic strain-dependent yield stress, $\sigma_{\gamma(\alpha)}(e^P)$ or the coefficient of thermal expansion, $\mu_\alpha(T)$ are those of the $\alpha$-phase. Likewise, a material which is completely of the $\beta$-phase has the mechanical properties of the $\beta$-phase. Now consider a third material which has an $\alpha$-phase fraction of $f_\alpha$ and a $\beta$-phase fraction of $f_\beta$. If only two phases are considered, then $f_\alpha + f_\beta = 1$, but the general case of $\sum_j f_j = 1$ for $j$ phases also holds. Assuming that both phases form a continuous, interconnected matrix throughout the material and assuming isotropic phase properties, then the yield stress of dual-phase material is $\sigma_{\gamma(\alpha\beta)}(e^P, f_\alpha, f_\beta) = f_\alpha \cdot \sigma_{\gamma(\alpha)}(e^P) + f_\beta \cdot \sigma_{\gamma(\beta)}(e^P)$. As a first approach, this linear mixing can be applied to all mechanical properties of the dual-phase material.

This adaptation of microstructure evolution to thermal-mechanical property evolution can be implemented in a thermal-mechanical finite element simulation as follows. As in the previous thought-experiment, consider a finite element having tabulated thermal-mechanical properties of the $\alpha$-phase and an element with the tabulated thermal-mechanical properties of the $\beta$-phase. Provided that the elements have the same dimensions, these two elements can be made to occupy the same volume, as shown in Figure 5.4, and coincidental nodes can be merged. This new, merged element can replicate a dual-phase material if the thermal-mechanical properties of the $\alpha$-element are multiplied by $f_\alpha$ and the thermal-mechanical properties of the $\beta$-element are multiplied by $f_\beta$. Since the nodes of the superposed elements are shared, the elements must deform together. Due to this linking, phenomena such as thermal expansion can be seen as generating internal stresses.
if $\mu_\alpha(T) \neq \mu_\beta(T)$.

This superposition of elements and node merging can be performed for an entire network of elements to give a complete, 3-dimensional mapping of the microstructure evolution. The strategy is not limited to dual phase systems; it can be applied to a material with $n$-phases by using $n - 1$ repetitions of the superpositioning procedure*. The calculation and mapping of the microstructure evolution during a welding thermal cycle is then implemented by following the dual-mesh strategy as described in section 5.2 with the modification that the mesh is duplicated and superimposed. For this initial thermal calculation, the phase fraction as a function of time and position is of course not known. The simplest way to handle this to let one element, say the $\alpha$-element, take on the experimentally measured, temperature-dependent thermal properties of the complete material. The thermal calculation is then performed with $f_\alpha = 1.0$ and $f_\beta = 0.0$ for the entire simulation. The use of a priori determined thermal properties was justified in section 5.2, since any given $\alpha$-element and its corresponding $\beta$-element share the same position, only one phase-field calculation needs to be performed for each position. These phase-field simulation results and the complete thermal profile are saved. Subsequently, the simulation is reset with the saved temperature data and phase fraction data being prescribed at the beginning of each time step at each element. The phase-dependent mechanical response of the material can then be calculated. The greatest challenge at this point is to gather temperature-dependent mechanical properties for a pure phase. This and other

*In this sense, the strategy could be considered as a ‘sibling-element’ strategy rather than a ‘twin-element’ strategy.
aspects, such as non-isotropic material properties and implications of the explicitly calculated microstructure morphology (banded structures, isolated precipitates, etc.) on the mechanical behaviour, is left to subsequent research.

Figure 5.5 shows the implementation of the twin-element strategy to a typical welding simulation of steel. The dual-mesh approach is carried out first to calculate the local microstructure evolution at each element. The saved temperature and phase fraction results are retrieved and mapped into the twinned mesh shown. Figures 5.5a and b show the temperature isosurfaces at 2 seconds and 5 seconds respectively. The implemented heat source is the surface adaptation of the Goldak ellipsoid distribution (see section 2.2.3) and the black isosurface represents the melting isotherm. Figures 5.5c and d show the ferrite fraction distribution at 2 and 5 seconds. Isosurfaces represent interpolations from the current local phase fraction at each element. The ferrite fraction is logically lowest near the weld pool and increases toward the cooler base material. Figures 5.5e and f show the distribution of austenite at 2 and 5 seconds. It should be noted that the $\gamma \rightarrow \delta$ phase transformation, melting, and solidification were not modelled in the current study. Therefore, even in the weld pool, the current implementation indicates $f_\gamma = 1$. The phase-field model can, however, calculate melting and solidification (see sections 2.3.2 and 2.3.3). Given sufficient information about fluid flow and other weld pool conditions, this same dual-mesh strategy can give information about the solidification microstructure.

The remaining chapters of this thesis are devoted to the development of physically-based material models, which founds the microstructure evolution in the dual-mesh strategy.
Figure 5.5: Results from the dual-mesh strategy coupled into the twin-element setting. Figures 5.5a and b show the temperature isosurfaces at 2.0 s and 5.0 s. The weld pool is indicated by the darkest isosurface. Figures 5.5c and d show the distribution of the ferrite phase fraction while figures 5.5e and f show the accompanying austenite phase fraction distribution. These phase distributions are the result of interpolation between phase-field calculations at each twin-element.
References


Part III

Implementation
Chapter 6

Grain Growth and Recrystallisation

6.1 Introduction

In this chapter, an analysis and model of the microstructure evolution in the heat affected zone (HAZ) of welded AISI316L is presented. AISI316L is an austenitic stainless steel which has only one solid state phase transformation, which takes place at less than 50 K under the melting temperature. This makes this steel an ideal medium to study interface motion and grain growth without the complications of phase transformations. The final stages of production of sheet AISI316L involves cold rolling and the accompanying introduction of stored strain energy. The recrystallisation phenomenon is therefore an important component to modelling efforts of the welded material.

A background of the physical phenomena is presented in section 6.2. The components and parameters of the material model are discussed in section 6.3 and followed by a description of the physical experiments in section 6.4. Results of the individual experiments and the accompanying simulation results are presented in section 6.5 and discussed in section 6.6.

6.2 Physical Phenomena

Grain growth in welding follows the same principles as outlined in sub-section 3.3.1 with one added aspect: thermal gradients in the workpiece can lead to significantly different growth conditions within short distances, even within distances shorter than the span of a single grain. A model including temperature dependent interface mobility coupled with thermal calculations of a sufficient spatial resolution is necessary in order to represent the grain growth in the HAZ of welded material.

As discussed in sub-section 3.3.2, the stored strain energy of a material can be reduced by recovery and by recrystallisation, both of which are thermally activated processes. The kinetics of the recovery process is dependent on the temperature and on the stacking fault energy of the material. According to dislocation theory, a low value of the stacking fault
energy, $\sigma_{\text{SF}}$, hinders dislocation climb and cross slip\(^1\) and thereby slows the recovery process. The stacking fault energy of austenitic steels is $\approx 20 \text{ mJ m}^{-2}$, compared to $\approx 170 \text{ mJ m}^{-2}$ for aluminium and $\approx 80 \text{ mJ m}^{-2}$ for copper.\(^2\) The low value of $\sigma_{\text{SF}}$ in AISI316L is also manifested by its creep resistant behaviour.\(^1,5\) This makes recovery a less-likely mechanism for the reduction of stored strain energy during the short welding thermal cycles and increases the importance of recrystallisation. Recalling the increased driving force behind interface motion due to the release of stored strain energy ($\nu_{\text{int}} = M |E_c - \sigma \cdot \kappa|$, see equation (3.12)), recrystallisation enables the strong grain growth observed in the HAZ of experimental weldments.

### 6.3 Model Construction

Physically-based modelling of the entire heat affected zone is a computationally formidable task. A strategy has been proposed to simulate a semi-continuous representation of the microstructure via discrete microstructure domains at the nodal points of a macroscopic finite element mesh.\(^4,5\) By calculating discrete points in the microstructure rather than a single, continuous microstructure, only a fraction of original microstructure needs to be modelled. Earlier studies showed that calculation times are directly proportional to the area of the calculated domain, leading to a significant reduction in calculation times with this dual-mesh strategy.\(^5\)

#### 6.3.1 Thermal Model

The temperature, thermal gradient, and heating or cooling rates are calculated with the finite element mesh and imposed as boundary conditions on microstructure calculations. The thermal calculations use a double-ellipsoid surface flux

$$q_i(x, y) = \frac{6\sqrt{3} f_i Q}{a b_i \sqrt{\pi}} \exp \left( -\frac{3 y^2}{a^2} \right) \exp \left( -\frac{3 y^2}{b_i^2} \right)$$

(6.1)

based on the Goldak volume source\(^6\) as presented in chapter 2. The subscript $i$ indicates the front or rear of the distribution, $q_i$ is the flux, $Q$ is the welding arc power defined by $\eta V I$, where $\eta$ is the energy transfer efficiency coefficient and $VI$ is the product of the voltage and current. The spatial coordinates are given by $x$ and $y$, which are the transverse and the weld direction respectively. The parameters $a$ and $b_i$ define the flux distribution width and length respectively. The division of the total welding power to the front and rear of the distribution is regulated by $f_i$. These thermal simulations are performed in a commercially available finite-element code.\(^7\) A total heat flux of 350 W with an efficiency of 90% was used to calculate the thermal conditions generated during autogenous arc welding described in section 6.4. Temperature dependent thermal conductivity was based on literature\(^8\) values for AISI316, and implemented as shown in figure 6.1. The increased conductivity above the solidus temperature reflects the phenomenon of mass transport in the weld pool, which aids the distribution of thermal energy. The thermal model has undergone extensive experimental validation for use with AISI316L.\(^9\) The microstructure calculations, the focus of this work, were carried out with the calculated thermal profile as input for phase-field simulations.
6.3. MODEL CONSTRUCTION

Figure 6.1: Temperature dependent thermal conductivity derived from literature values.

6.3.2 Material Model

The core of the phase field model is based on the definition of a so-called state variable over the entire computational domain. It can be dependent on composition, orientation, or long-range atomic order. The phase-field method has also been adapted for multiple phase calculations, which have been addressed in the literature\(^\text{10, 11}\) and in chapter 2 of this thesis. This concept allows each grain to have uniquely defined properties, such as the value of stored strain energy. The multi-phase phase-field code used here, MICRESS\(^\text{11}\), is developed by ACCESS e.V., Aachen, Germany.

The initial microstructure is constructed using randomly positioned grains with a grain size variation based on measured grain sizes. The average initial grain size is set to 15 \(\mu m\) to match with experimental measurements in the base material. Physical material properties at the microscopic level are derived via the theoretical considerations presented in sections 3.3.1 and 3.3.2 or from published literature values. The migrational activation energy, \(Q_m\), as presented in section 3.2 is based on the activation energy for self-diffusion in austenitic iron, \(Q_{ad}\), minus the activation energy for vacancy creation, \(Q_v\). \(Q_{ad}\) has been measured\(^\text{11, 12}\) to be approximately 300 kJ mol\(^{-1}\) and \(Q_v\) has been theoretically derived\(^\text{13}\) to be approximately 100 kJ mol\(^{-1}\). This delivers an initial estimate for \(Q_m\) of 200 kJ mol\(^{-1}\). The mobility model is implemented using \(d = 2.6\) A and \(v_D = 6 \cdot 10^{13}\) Hz.

To derive values for the stored strain energy in the material in the as-received state, the combined effect of the cold-rolling and the stress-relief heat treatment during production of the AISI316L sheet material considered. Although the release of stored strain energy during the stress-relief treatment was likely small due to AISI316L’s low stacking fault energy, any possible recovery was accounted for by measuring the yield stress in the as-received state \((\sigma_r = 300\) MPa\). Using the typical value for the shear modulus of AISI316L \((G = 75\) GPa\) and equations (3.9) and (3.10), a dislocation density of \(\rho_{\text{init}} = 10^{12}\) m\(^{-2}\)
was derived, leading to a stored strain energy of $E_s = 2.4 \times 10^6$ J m$^{-3}$. Assuming random orientation of the grains, a uniform distribution of the stored strain energy between $2.0 \times 10^6$ and $3.0 \times 10^6$ J m$^{-3}$ was implemented. In order to host the nucleation of recrystallised grains in the simulations, a minimum stored strain energy of $2.5 \times 10^6$ J m$^{-3}$ was required. The value for the grain boundary energy is based on the published value for AISI304 of $\sigma_{gb} = 0.835$ J m$^{-2}$. Following the theory that the nuclei of recrystallised grains are actually sub-grains with highly localised deformation, nuclei are given an initial size of 3 $\mu$m.

### 6.4 Physical Experiments

AISI316L (by weight percent, Cr 16.6, Ni 10.5, Mo 1.8, Mn 1.3, Si 0.3, C < 0.03) was received as 2 mm sheet. Samples were sheared into 100 mm by 120 mm sections. In standard production, such sheet material is cold-rolled and subjected to a ‘Stress-Relief and Stabilize’ (SRS) heat treatment. The SRS heat treatment involves heating samples to 1158 K for 2 hours followed by a slow cool to 948 K before furnace-cooling to room temperature, which allows the material to undergo partial recovery. To observe grain growth rates without initiating recrystallization, a set of samples received an additional SRS heat treatment and are referred to as ‘SRS’ samples in this work. A second set of samples was annealed, and are thus referred to as ‘ANN’ samples here. The annealing heat treatment involved heating to 1373 K for two hours and a subsequent furnace-cool. A third set of as-received samples served as the control set. The thermal cycles of the SRS and the anneal treatment are compared with the thermal cycle experienced by a material point 100 $\mu$m from the fusion line during gas-tungsten-arc (GTA) welding in figure 6.2.

GTA welds were made on three SRS samples, three ANN samples, as well as three as-received samples. The welding power was 350 W (35 A, 10 V) and the constant welding velocity was $v_w = 2$ mm s$^{-1}$. Other welding parameters are listed in table 6.1. These parameters lead to welds of partial penetration, a typical example of which can be seen in figure 6.3. Before welding, the surfaces of SRS and ANN samples were polished with 240-grit silicon-carbide paper in order to remove the oxide layer. All surfaces were cleaned with alcohol immediately prior to welding.

<table>
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<th>Table 6.1: Welding Process Parameters.</th>
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<td>Welding Electrode</td>
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<td>Torch Polarity</td>
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<td>Arc Length</td>
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<td>Shielding Gas</td>
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<td>Shielding Cup Diameter</td>
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Cross-sections of the weld and HAZ microstructure were made perpendicular to the welding direction. The final polishing step was made with a 0.06 $\mu$m diamond polishing compound and etched with diluted Villela (10 ml HNO$_3$, 20 ml HCl, 30 ml glycol) for 25 minutes. Grain sizes were measured via the chord intersection method along arcs which followed the contour of the fusion line at the desired distance.
6.5 Results

Figure 6.4 shows the as-received microstructure next to the microstructure resulting from the SRS heat treatment and microstructure after annealing. The average grain size in the as-received samples was measured to be 14.9 μm with a standard error of 0.4 μm. The average grain size after the SRS heat treatment increased to 18.5 μm with a standard error of 0.6 μm. The annealing heat treatment resulted in an average grain size of 75.8 μm with a standard error of 4.9 μm.

The activation energy for grain boundary mobility was approximated with the considerations in section 6.3. The simulations of the SRS samples assume that the SRS thermal cycle kept the material at a low enough temperature so as not to initiate recrystallisation. The average and standard error of the measured final grain sizes after the SRS heat treatment are shown in figure 6.5 along with simulation results for a range of $Q_m$ values. The choice of $Q_m = 197.5$ kJ · mol$^{-1}$ was made based on how the final simulated grain size values compared with this and subsequent experimental results.

Simulations of the annealing process included recrystallisation. The temperature at which strain-free, recrystallised grains were permitted to start forming was set to 1300 K in all simulations. This choice will be further discussed in section 6.6. The density with which the recrystallised grains were allowed to form was $5.77 \cdot 10^{-1}$ μm$^{-2}$, or 40 recrystallised grains in a phase-field domain of 262.5 μm x 262.5 μm. Figure 6.6a shows the progression...
of the average grain size as a function of time during the annealing treatment. The sudden change in grain size after 4500 s is caused by the introduction of recrystallised grains. This time span is magnified in figure 6.6b.

Experimental welding was carried out on the SRS and ANN samples, as well as on material in the as-received state. Accompanying simulations of the microstructure evolution were made for microstructure at 100 µm, 150 µm, 200 µm, 350 µm, and 500 µm from the fusion line for the SRS, ANN, and as-received cases. Simulations of the HAZ in material that was previously heat treated (SRS and ANN samples) used the results from the heat treatment simulations as the base material. Therefore, for the SRS-case, the same post-SRS microstructure was assumed for all positions. Recrystallised grains were formed in the given microstructure as the local temperature exceeded 1300 K. Figure 6.7a shows results of measured grain sizes as a function of distance from the fusion line (data points with error bars), as well as results of the simulated microstructure domains (points joined by a dashed line).

Experimental welds on the ANN samples produced no noticeable grain growth in the HAZ. Simulated microstructures from the annealing heat treatment were subjected to the welding thermal cycles from the same selected points as for the SRS-case. Since the microstructure was annealed, the critical stored strain energy was not present and no further recrystallisation occurred. The simulations of the microstructure at the selected points exhibited no grain growth, as shown in figure 6.8a. Some experimental samples actually showed a decrease in the grain size next to the fusion zone due to partial melting of large grains, seen in figure 6.8b.

The experimental welds were also performed on material in the as-received state.
The simulated base material microstructure was the same as the microstructure used for simulating the heat treatments. The simulated progression of the average grain size with time during the welding thermal cycle is shown in figure 6.9a. The comparison of the final calculated grain size at various positions in the HAZ with measured grain sizes in the experimental HAZ is given in figure 6.9b.

Figure 6.10a-f shows the simulated morphological evolution of the microstructure at a position 150 μm from the fusion line in an as-received sample. Brighter shades indicate higher stored strain energy. The initial microstructure is shown in figure 6.10a. After 0.5 s, the temperature has exceeded 1300 K and the first recrystallised subgrains can be seen in figure 6.10b. Figure 6.10c shows the recrystallised grains at a size comparable with that of the original grains, some of which are on the verge of being completely consumed. Figure 6.10d illustrates the non-uniform growth in the calculated plane as a result of the distribution of stored strain energy. Significant impingement of the recrystallised grains is shown in figure 6.10e, which corresponds to the point in time at which grain growth proceeds at a slower rate in figure 6.9a. The final microstructure at a position 150 μm from the fusion line is shown in figure 6.10f.

6.6 Discussion

In the microstructure calculations, it is of central importance to determine whether the active mechanism for the microstructure evolution is grain growth or a combination of grain growth and recrystallisation. If recrystallisation plays a role, the temperature at which recrystallised grains begin to form and the density of these grains must also be determined.

To decide whether grain growth is the sole mechanism for microstructure evolution, the change in the total interfacial energy of a representative volume can be compared with the thermal energy provided to that same volume during a given thermal treatment. The change in interfacial energy, $\Delta E_{\text{int}}$, in the considered volume can be quantified by the change in grain boundary area. Approximating the grains as spheres, for a volume of $V^3$, the change in interfacial energy can be expressed as

$$\Delta E_{\text{int}} \approx 6 \cdot \sigma_{\text{int}} \left( \frac{1}{D_o} - \frac{1}{D_f} \right),$$  (6.2)
where $D_i$ and $D_f$ are the initial and final average grain sizes and $\sigma_{\text{tot}}$ is the interfacial energy. The thermal energy, $\Delta E_{\text{therm}}$, provided to the same volume, $V$, during a heat treatment can be quantified by considering the product of the specific heat and the local temperature, integrated over the duration of the process. This is expressed as

\[
\frac{\Delta E_{\text{therm}}}{V} = \int_{t_i}^{t_f} c_p(T) \cdot T(t) \, dt,
\]

where $c_p(T)$ is the temperature dependent specific heat, and $T(t)$ is the local temperature as a function of time, $t$. This thermal energy is dissipated among a number of thermally activated mechanisms, including chemical diffusion, dislocation annihilation, and diffusion of the thermal energy to the surrounding material. If the density of the considered material volume ($V = I^3$) is approximated as constant during the thermal cycle, then the energy described by equation (6.3) can be expressed as energy per unit volume for the duration of the process and can then be compared with the energy described by equation (6.2).

If this analysis is carried out at a series of positions in the HAZ of an as-received sample, an interesting trend can be observed. A calculated thermal cycle for positions 100 $\mu$m, 150 $\mu$m, 200 $\mu$m, 300 $\mu$m, and 400 $\mu$m from the fusion line were compared with grain measurements at the same points. Grain growth is a thermally activated process, and it is therefore reasonable to expect that positions that received more thermal energy (i.e. reached a higher temperature) also released more interfacial energy during the thermal cycle. Figure 6.11 shows the results from these measurements and calculations for the
6.6. DISCUSSION

Figure 6.6: Figure 6.6a shows the calculated average grain size evolution during the annealing heat treatment. The high growth rate (in the dashed box, magnified in figure 6.6b) during recrystallization is followed by a period of secondary grain growth. The upper plateau corresponds to the time range at which the sample cools and the temperature dependent mobility is reduced. The final measured grain size is shown with error bars. Figure 6.6b shows a more detailed view of the calculated growth kinetics during recrystallization. A reduction in the average grain size is observed with the introduction of recrystallised grains. The high growth rate is reduced once recrystallised grains impinge against one another and the fraction of recrystallised material reaches 1.0.

Figure 6.7: Grain size is plotted as a function of distance from fusion line in the GTA welds of the partially-recovered (SRS) samples is shown in figure 6.7a. Simulation results are joined by the solid line. A micrograph of the HAZ of the SRS samples is given in figure 6.7b.
energy in a volume of 8000 $\mu m^3$ ($l = 20 \mu m$). The difference in scale in the quantities in figure 6.11 can be brought into perspective when considering that the total amount of interfacial energy in the volume before welding was only $2.4 \times 10^{-9}$ J. Indeed, a direct proportionality can be seen at the points furthest from the fusion line. However, at points closer to the fusion zone, the relationship changes. It can be argued that this is simply an effect of the thermal energy being proportional to $T$ while the release of interfacial energy is dependent on $\exp(-Q_m(kT)^{-1})$, but if this were the case, a single $Q_m$ would provide fitting grain growth kinetics for both the SRS simulations and the ANN simulations. However, simulating the ANN thermal cycle with the optimum $Q_m$ for the SRS simulations (see figure 6.5) while not allowing recrystallisation resulted in a final grain size much lower than the measured grain size from the ANN samples. This is the first indication that an additional mechanism for microstructure evolution, such as recrystallisation, has been activated in these welds.

Another indication that recrystallisation can be activated in the as-received material is gained by inspecting the progression of grain size in the HAZ of annealed samples. The annealing heat treatment is designed to initiate and complete the recrystallisation process. Assuming that this process produces a virtually strain-free microstructure, recrystallisation cannot take place in subsequent heat treatments. The grain size in the HAZ of the annealed samples did not exhibit noticeable grain growth next to the fusion zone (see figure 6.8) compared to the thermal energy provided, which was the same as the thermal input in figure 6.11. In fact, due to the large variation in grain size after the annealing (but before welding), a distinct growth trend towards the fusion zone was not evident.

The grain growth model, based on the temperature dependent grain boundary mobility, was based on the theory presented in subsection 3.3.1. The SRS heat treatment provided the ideal setting to examine grain growth without the significant release of strain energy associated with recrystallization. A truly temperature dependent model should be
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![Graphs of grain size evolution during welding and grain size distribution through the HAZ.](image)

(c) Micrograph of the HAZ in as-received material.

Figure 6.9: Figure 6.9a shows calculated average grain size at given distances from the fusion line versus welding time. A reduction in the average grain size is observed with the nucleation of new grains at approximately 0.5 seconds. Figure 6.9b illustrates grain size versus distance from fusion line in the GTA welds of the as-received samples. Simulated grain size values are joined with a spline approximation line. A micrograph of the HAZ in as-received material is provided in figure 6.9c.
Figure 6.10: Representations of the microstructure (as-received state) at 150 μm from the fusion line for various times through the welding thermal cycle (from left to right, top to bottom). Shading in the figures indicates amount of stored strain energy with darker shading representing lower values of stored strain energy. Figure 6.10a shows the initial microstructure while figure 6.10b shows the first signs of recrystallization at t = 0.5 s. At t = 1.4 s, recrystallised grains have reached the approximate size of the original grains, shown in figure 6.10c. Figure 6.10d (t = 2.0 s) illustrates distinctly non-uniform growth. Figure 6.10e represents the microstructure at t = 2.5 s with impingement of recrystallised grains. Figure 6.10f shows the final microstructure.
valid for both the long holding times of the heat treatment as well as the short, intense
growth periods associated with welding. The one value that was difficult to determine a
priori was the activation energy for atomic migration, $Q_m$. Comparison with experimental
results of the SRS- and ANN-cases lead to an activation energy of $Q_m = 197.5$ kJ mol$^{-1}$.
The mobility calculated here thus ranges from $M(900 \text{ K}) = 7.8 \times 10^{-17}$ m$^4$ (Js)$^{-1}$ to
$M(1600 \text{ K}) = 4.5 \times 10^{-12}$ m$^4$ (Js)$^{-1}$ and produces finite growth kinetics that are appro-
riate for heat treatments, as well as the growth associated with the short thermal cycles
which are characteristic of welding.

The recrystallization component of the model presented in subsection 3.3.2 was also
implemented according to the given theory, however the recrystallization temperature
and the nucleation density could not be gleaned from theoretical considerations and relied
on experimental observation and deductive reasoning. The recrystallization temperature
is not characteristic of the material per se, but strongly dependent on the mechanical
and thermal history that the material has experienced.\textsuperscript{1, 15, 16} From the heat treatment
experiments, abnormal grain growth associated with recrystallization was not observed in
the partially-recovered samples, which stayed below 1158 K (SRS heat treatment). From
these and the annealing results, it can be concluded that the recrystallization temperature
lies between 1158 K and 1373 K (the holding temperature of the annealing treatment).
From the location of the material point furthest from the fusion zone which displays
evidence of recrystallization, and by using interpolation within the calculated thermal
field, the recrystallization temperature was estimated to be 1300 K.

Considering the nucleation density of recrystallised grains lead to a serendipity of
the usually challenging, highly inequilibrated thermal cycles associated with welding.
Assuming that recrystallization indeed takes place next to the weld pool, the final grain
density next to the weld pool is in fact the ideal location to measure nucleation density since secondary grain growth has minimal time to develop. This allowed the final grain density at approximately 100 μm from the fusion line in an as-received sample to be directly used as the nucleation density for recrystallization. At distances of less than 100 μm from the fusion line, larger grains are often partially melted. From analysis of micrographs, the nucleation density in the analysed surface was estimated as $\rho_{nuc} = 5.8 \times 10^{-4} \, \text{μm}^{-2}$.

This nucleation density was used for the calculations of the annealing heat treatment. The microstructure was modelled with an initial grain size of 15 μm. Nucleation of recrystallised grains occurred once the sample had reached 1300 K, which occurred after 4500 s. As seen in figure 6.6a, the newly nucleated grains contributed to a temporary drop in the average grain size, a more detailed view of which is shown in figure 6.6b. This was followed by a period of strong growth which continued until the recrystallised grains impinged against one another. After impingement, the microstructure followed standard grain growth until the heat treatment came to an end and the sample was cooled. Once the sample cooled to below approximately 1000 K, further grain growth ceased.

The calculated microstructure after the annealing thermal cycle exhibited a significant range in grain sizes, as did the experimental microstructure. The measured grain sizes from the experimental heat treatments are shown, with error bars, on the right of figure 5.5a and 6.6a. This range in grain sizes has consequences for the measured grain size in the HAZ of samples that were subsequently welded. Experimental measurements in figure 6.5h show higher growth close to the fusion line than the calculated microstructure. Although the actual microstructure in the SRS samples started with a large range of grain sizes, the simulations start with a different grain size distribution. It is likely that the apparent additional growth close to the fusion zone in the experimental welds is due to very small grains being consumed. As-received samples, on the other hand, started with an equiaxed microstructure with very little variation in the measured grain sizes. This allowed the simulations with a homogeneous grain size distribution to be more representative of the initial experimental conditions.

The modelled microstructure morphology for a material point 150 μm from the fusion zone is shown in figure 6.10. Figure 6.10a shows the initial microstructure with lighter shading representing higher amounts of stored strain energy, $E_s$. Figure 6.10b shows the microstructure at $t = 0.5$ s, as the first recrystallised grains appear along grain boundaries and triple junctions of grains with the highest stored strain energy. Here, and in the following figures, the non-homogeneous distribution of recrystallised grains is in agreement with the observations of Martinsen et al. and distinguishes this model from standard JMAK models in which a random distribution of nuclei and homogeneous growth are underpinning assumptions.

Figure 6.10c, at $t = 1.4$ s, shows the recrystallised grains reaching the approximate size of the original microstructure. Another important feature of these simulations, and a distinction from JMAK models, is the ability to represent non-isotropic growth of recrystallised grains, driven by the distribution of stored strain energy. This is determined by the initial stored strain energy distribution which, in turn, dictates the degree with which free energy can be released via recrystallization in a given direction. The non-isotropic growth can be seen in figure 6.10d ($t = 2.0$ s) and the following frames. At $t = 2.5$ s, impingement of recrystallised grains against one another begins to have a damping effect on the growth kinetics (see figure 6.9a) and evolves the microstructure into one with longer, flatter interfaces (figure 6.10e).
6.7 Conclusions

An experimentally validated adaptation of the Goldak double-ellipsoid flux distribution is implemented for the simulation of autogenous arc welding of AISI316 samples. The microstructure in the heat affected zone was simulated with the phase-field method. Simulations of two separate heat treatments and of the subsequent welding were also carried out. An appropriate expression for the interface mobility, $M$, was found to be $M = \frac{(d^4 \nu_0)}{(kT)} \cdot \exp(-Q_m/(RT))$ with $d$ for AISI316 being 2.6 Å and $Q_m = 197.5$ kJ mol$^{-1}$. The phenomenon of recrystallization was found to play an essential role in the evolution of the microstructure. Due to the short duration of the welding thermal cycle, it was found that the heat affected zone of AISI316 could provide the nucleation density for recrystallised grains.
References


Chapter 7

Phase Transformation: Low-Carbon Steel

7.1 Introduction

In this chapter, simulations of the phase transformations occurring in a low-carbon manganese steel (AISI1005) during welding will be compared with synchrotron measurements from the literature. After a brief review in section 7.2 of the physical phenomena involved (details can be found in chapter 3), the model for the welding heat source and of the material microstructure model is described in section 7.3. The experimental apparatus and procedure is reviewed in section 7.4, followed by a comparison between results from the simulations and experimental findings in section 7.5. A detailed analysis of the simulated microstructure evolution at selected points in the heat affected zone (HAZ) next to the weld is presented and discussed in section 7.6.

7.2 Physical Phenomena

During the welding of a low-carbon steel, grain growth and recrystallisation have a much smaller influence on the final microstructure than in the AISI316L welds studied in chapter 6. The greater factor in the evolving microstructure is the nucleation and growth of austenite upon heating and the nucleation and growth of ferrite (among other phases) upon cooling. The austenitisation transformation follows the same theoretical basis as outlined in section 3.4.2 of this thesis, with the extension of considering a starting microstructure of two phases instead of the one phase considered in the theory. Upon cooling, the carbon enrichment of the remaining austenite has a significant effect on the motion of the ferrite/austenite interface, as outlined in section 3.5.
7.3 Model Construction

7.3.1 Thermal Model

Following the dual-mesh strategy proposed in chapter 5 and earlier work, a heat source model was developed to represent the experimental gas-tungsten arc (GTA) welding source used by Elmer et al. Due to the complexity of the experimental setup, no temperature measurements could be made. Elmer et al. presented a heat source model involving fluid flow in the melt pool with results that compared well with a metallographic investigation of the weld pool. However, after a closer investigation of calculated temperatures in the HAZ and the measured phase fractions, some discrepancies were found. It was also noted that the published thermal model used a temperature-independent thermal conductivity for the solid material. This motivated the thermal modelling efforts in this work, where the double-ellipsoid heat flux distribution proposed by Goldak was adapted to a surface flux, as introduced in chapter 2. The essence of the model is to distribute the heat flux of the welding arc, $q_i$, over the area under the arc via

$$
    q_i(x, y) = \frac{6\sqrt{3}f_i Q}{a b \pi \sqrt{\pi}} \cdot \exp \left( -\frac{3 x^2}{a^2} \right) \cdot \exp \left( -\frac{3 y^2}{b^2} \right)
$$

(7.1)

where $x$ and $y$ define the transverse and welding direction while $a$ and $b_i$ define the flux distribution width and length respectively. As the name indicates, the double-ellipsoid flux distribution defines a front and rear half distribution for the flux, which is identified by the index $i$. Here, $i = t$ specifies parameters for the front ellipsoid and $i = r$ labels parameters for the trailing ellipsoid. The division of the total welding power to the front and rear of the distribution is regulated by $f_i$. $Q$ is the total power defined by $\eta \mathcal{V} \mathcal{I}$, where $\eta$ is the energy transfer efficiency coefficient and $\mathcal{V} \mathcal{I}$ is the product of the voltage and current. The implemented values for the heat source model parameters are given in table 7.1.

<table>
<thead>
<tr>
<th>$a$ [mm]</th>
<th>$b$ [mm]</th>
<th>$c_i$ [mm]</th>
<th>$f_i$</th>
<th>$c_r$ [mm]</th>
<th>$f_r$</th>
<th>$\mathcal{V} \mathcal{I}$ [W]</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>2.0</td>
<td>4.75</td>
<td>1.2</td>
<td>4.50</td>
<td>0.80</td>
<td>1925</td>
<td>0.93</td>
</tr>
</tbody>
</table>

This approach has been extensively used to provide accurate temperature results in the HAZ. The purpose in this work was not to generate an intricate thermal model with fluid flow aspects, but rather to develop a model which would feed the microstructure simulations in the HAZ with the appropriate thermal boundary conditions. The double ellipsoid distribution of the heat flux was implemented in MSC.Marc, a finite element package. A crucial parameter was the energy transfer efficiency between the arc and the workpiece. $\eta$, which was adjusted to produce the best agreement between synchrotron determination of the HAZ dimensions and the calculated thermal field. Temperature dependent thermal conductivity was estimated from literature values for AISI1006 and implemented as shown in figure 7.1. The increased conductivity above the solidus temperature reflects the phenomenon of mass transport in the weld pool which aids the distribution of thermal energy.
7.3. MODEL CONSTRUCTION

![Graph showing thermal conductivity vs. temperature](image)

Figure 7.1: The implemented temperature dependent thermal conductivity derived from literature values for AISI1006.

7.3.2 Material Model

A model for the development of the microstructure during the thermal cycle was constructed based on the experimental base material presented in the literature. This consisted of a ferrite matrix with approximately 2% pearlite at the grain boundaries. The average ferrite grain size was measured to be 22 μm, while the pearlite colonies were approximately 5 μm in size.

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Cn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.31</td>
<td>0.05</td>
<td>0.18</td>
<td>0.10</td>
<td>0.11</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 7.2: Alloying elements in wt% (Balance Fe).

The thermodynamic driving forces for phase transformation are considered to be dependent on temperature and local composition. The overall composition of AISI1005 is given in table 7.2. These elements were considered when calculating the equilibrium relation between possible phases over the temperature range experienced in the heat affected zone. Considering the diffusivity of interstitial carbon as being several orders of magnitude higher than that of the other alloying elements, a Fe-C para-equilibrium phase diagram (see figure 7.2) was constructed with the TCFE2 database and ThermoCalc®. For the nominal composition, an A1-temperature of 993 K and an A3-temperature of 1158 K were calculated.

This thermodynamic construction was implemented in the MICRESS® phase-field
Figure 7.2: The calculated Fe-rich side of the phase diagram for AISI1005 under para-equilibrium conditions with the linearized form used in implementation as a dashed overlay. Note the meta stable extension of the line separating α/α + γ.

The code, which is based on the work of Steinbach et al.,\(^7\,^8\) An overview of phase-field models can be found in section 2.3.2 of this thesis and in the literature.\(^9\) A distinguishing feature of the approach of Steinbach et al. is the multiple phase setting. The interface mobility theory developed in section 3.2 produced an expression for temperature- and phase-dependent mobility, \(M_{ij}\), via

\[
M_{ij} = M_0 \cdot \exp\left( -\frac{Q_{ij}}{kT} \right) \quad \text{with} \quad M_0 = \frac{d_{ij}^3 \nu_D}{kT},
\]

(7.2)

where \(Q_{ij}\) is the activation energy for atomic motion between the two phases, \(d_{ij}\) is the average lattice spacing of phase \(i\) and phase \(j\) being separated by the interface in question, and \(\nu_D\) is the Debye frequency of the host material. Mobilities of the various interfaces were treated individually based on lattice dimensions of the phases in question, as shown in table 7.3. Values for \(d_{ij}\) were calculated with equation 3.3. The parameter for pearlite was thus an average between the atomic volume of Fe in ferrite and in the orthorhombic lattice for \(\text{Fe}_3\text{C}\). Phase-dependent interfacial energies, \(\sigma_{ij}\), were derived from the literature,\(^10\) and are also shown in table 7.3.
7.3. Model Construction

Table 7.3: Mobility and interfacial energy parameters for AISI1005.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha : \alpha$</th>
<th>$\alpha : \gamma$</th>
<th>$\gamma : \gamma$</th>
<th>$\gamma : \gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{ij} [\text{Å}]$</td>
<td>2.4</td>
<td>3.2</td>
<td>2.5</td>
<td>3.3</td>
</tr>
<tr>
<td>$Q_{ij} [\text{kJ mol}^{-1}]$</td>
<td>150</td>
<td>200</td>
<td>162.5</td>
<td>162.5</td>
</tr>
<tr>
<td>$\sigma_{ij} [\text{J m}^{-2}]$</td>
<td>0.8</td>
<td>0.9</td>
<td>0.3</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Considering figure 7.2, the driving force for the austenitisation of ferrite is derived by

$$
\Delta G_{\alpha \gamma} = -S_{\alpha \gamma} \cdot \Delta T(\text{C}) ,
$$

where $\Delta S_{\alpha \gamma}$ is the entropy of fusion between ferrite and austenite and is calculated by dividing the enthalpy change of transformation by the transformation temperature. $\Delta T(\text{C})$ is the difference between the local temperature and the temperature of the composition dependent meta-stable extension of the line separating the single phase $\alpha$ region and the two phase $\alpha : \gamma$ region, shown in figure 7.2. However, if austenite nucleates from Fe$_3$C, then $\Delta T(\text{C})$ is the difference between the local temperature and the line marking the upper stability limit of Fe$_3$C, also known as the Al-temperature. Logically, the expression for $\Delta G_{\text{Fe}_3\text{C}-\gamma}$ would require $\Delta S_{\text{Fe}_3\text{C}-\gamma}$. These considerations apply for the $\gamma \rightarrow \alpha$ transformation upon cooling.

Using the phase-dependent interface mobility and the locally defined driving force behind interface motion, the expression for interface velocity followed as

$$
v_{\text{int}} = M_{ij} \left[ \Delta G_{ij} - \alpha_{ij} \cdot \kappa \right] ,
$$

where $\kappa$ is the local interface curvature, as explained in section 3.3.1 of this thesis.

Although pearlite is a collective term for alternating lamellae of ferrite and cementite, the computational cost required to resolve the sub-micron lamella would have been prohibitive. Instead, an ‘equivalent pearlite’ was proposed. This phase is modelled as having the eutectoid composition (0.7 wt% C), with an initially homogeneous carbon distribution. The surrounding ferrite matrix was given an initial carbon concentration of 0.02 wt%, leading to an overall carbon concentration of 0.05 wt%. If the pearlite lamella were to be modelled explicitly, this would require a grid spacing in the order of $\Delta x = 10^{-9}$ m which translates into a grid density of $10^9$ µm$^{-2}$ compared to the current grid density of 25 µm$^{-2}$. This is not only significant for calculation times, but due to memory size limitations, many computers would not be able to initialise the grid let alone carry out the calculations. The approximation of the pearlite phase also had ramifications for the thermodynamics. In deriving the interaction between pearlite and austenite, the Fe$_3$C line in the standard equilibrium phase diagram is shifted from 6.7 wt% C to the eutectoid composition for AISI1005 of 0.7 wt% C. The slight increase of C-solubility in ferrite with rising temperatures below the Al-temperature is also incorporated. Finally, it should be mentioned that the line separating the $\gamma$ and Fe$_3$C + $\gamma$ regions extends past the eutectic point into the $\alpha +$ Fe$_3$C region. Upon reaching the temperature for austenite nucleation, this extended line defines the increased driving force for austenite to consume C-rich pearlite.
Since the starting microstructure was not a single phase nor chemically homogeneous, the relations between grains and potential nucleation sites developed in chapter 4 were adapted. Here, important information about the density of potential nucleation sites could be gathered with the aid of pre- and post-weld micrographs. A micrograph of the partially-transformed region (7.5 mm from the weld centre) gives the most direct information about the cooling cycle, shown in figure 7.3. This micrograph shows localised regions, measuring approximately 25 μm in diameter, of ferrite grain refinement around former pearlite colonies. Due to the high cooling rates in the HAZ and the short period of time that the partially transformed region was above critical temperatures, it can be concluded that these images give an accurate impression of the microstructure appearance only seconds after transformation. Since grain growth and grain agglomeration occur at significantly lower rates, it can be concluded that the grain density in the refined regions is in fact the nucleation density of the ferrite in austenite upon cooling. This is one of the crucial parameters for the microstructure model and was implemented such that the modelled microstructure domain could host a maximum ferrite nucleation density of $2.8 \cdot 10^{-3} \text{ mm}^{-2}$. The nucleation density of the austenite upon heating is also of importance. This parameter is not as directly visible as the ferrite nucleation density. However, assuming that each ferrite nucleus was hosted by an average of one austenite parent grain, the number of austenite nuclei should be comparable to number of ferrite nuclei. Analysis of the fully transformed region suggested a slightly lower austenite grain density leading to the implementation of an austenite nucleation density of $2.2 \cdot 10^{-3} \text{ mm}^{-2}$. At the time of performing this study, the nucleation model was not as advanced as that presented in chapter 4. Here, the time necessary for transformation, gathered from the synchrotron measurements, dictated a nucleation rate of 90 nucleations per second. For a pure ferrite microstructure of the measured grain size, implementation of the procedures in chapter 4 would provide a total of 216 potential nucleation sites ($N_f = 126$, $N_e = 84$, $N_c = 6$). This would produce a nucleation rate lower than 90 per second. However, considering the presence of pearlite with its higher density of interfaces to provide more nucleation sites, a nucleation rate of 90 per second is not unrealistic.

Figure 7.3: Micrograph of the partially transformed region in the HAZ, approximately 7.5 mm from the weld centre. A ferrite matrix can be seen with grain refinement around former pearlite colonies. This refined grain density gives important parameters for the nucleation model.
7.4 Physical Experiments

The simulations presented in this chapter were based on experimental work by Elmer et al. Autogenous welds were made on a forged cylindrical bar of AISI1005, machined to a diameter of 10.2 cm and a length of 12.7 cm. Welding current oscillated between 90 and 130 A at 300 Hz to combat weld pool sloshing and improve arc positioning, while the voltage remained at 17.5 V. The cylinder was rotated such that the welding velocity was constant at 0.6 mm s⁻¹.

The in-situ spatially resolved X-ray diffraction experiments reported here were performed during welding using the 31-pole wiggler beam line, BL 10-2 at the Stanford Synchrotron Radiation Laboratory with SPEAR (Stanford Positron-Electron Accumulation Ring) operating at an electron energy of 3.0 GeV and an injection current of 100 mA. In these experiments, a focused monochromatic synchrotron X-ray beam was passed through a 260 μm tungsten pinhole to render a sub-millimeter beam on the sample at an incident angle of approximately 25°. A line detector was used to record diffraction peak intensities over a 2θ-range of 25-55°. This 2θ range was optimized to contain a total of six diffraction peaks, three from the bcc phases (α-Fe or δ-Fe) and three from the fcc phase (γ-Fe). During a typical measurement, 40 diffraction patterns were gathered at intervals of 250 μm along a pre-determined path, spanning a range of 10 mm through the HAZ. The accuracy of the positioning of the SRXRD beam with respect to the fusion boundary for a given weld is ±0.5 mm. This estimate considers the initial positioning the X-ray beam, and dynamic fluctuations in the fusion boundary. Further experimental details have been presented in the literature.

7.5 Results

7.5.1 Thermal Field

Parameters for the double-ellipsoid volume distribution of the thermal energy flux were taken directly from the reported weld pool dimensions. The efficiency of the thermal energy transfer required an estimation based on agreement with the published metallographic study and thermal modelling. Setting the efficiency, η, to 0.93 produced the best agreement with experimental weld pool geometry. The in-situ synchrotron measurements in figure 7.4 also gave an indication of the breadth and length of the region trailing the arc which was above the A1-temperature. The thermal model presented here produced better agreement with the width of the experimental HAZ, but left room for improvement on the trailing length of the HAZ. This could be due to a number of factors, such as errors in the estimates for convectional and radiation heat losses to the atmosphere, but these differences are not of primary relevance to the present discussion and are not considered further in this work.

7.5.2 Phase Transformation

Figure 7.5a shows the initial microstructure in the welded AISI1005 samples. The simulated evolution of the microstructure during welding is shown in figure 7.5b - g. As the temperature rises above the austenitisation temperature, austenite nucleation commences. A factor in determining the location of the austenite nuclei is the introduction
of new interfacial energy, which assists nucleation at higher order junctions and then at binary grain boundaries, as discussed in chapter 4. The growth rate of austenite next to the pearlite is significantly higher than between ferrite grains due to the localised carbon concentration, as seen in figures 7.5c, e and g. Diffusion within the phases is controlled by temperature- and phase-dependent calculations. At peak temperatures, most of the austenite regions have a homogenous carbon concentration, but due to the relatively low diffusion coefficients in austenite, some of the larger regions still display a noticeable concentration gradient, shown in figure 7.5e. As the domain cools below the A3-temperature and through the two-phase temperature range, austenite gives way to the nucleation and growth of ferrite at austenite grain boundaries. Carbon is pushed ahead of the growing ferrite phase front, resulting in line, clustered regions of carbon-rich austenite, displayed in figures 7.5f and g. The transformation of this austenite to pearlite or bainite was not modelled in this work.

The inherent relation between the thermal simulations and the microstructure simulations can be seen in figure 7.6. Slight variations in the arc efficiency factor, \( \eta \), influenced the thermal cycle and, in turn, the simulated phase transformations. The value for \( \eta \) giving the best agreement between simulated and experimental weld pool dimensions also gave the best agreement between simulated and experimentally measured phase fractions. Figure 7.6a shows the influence of varying \( \eta \) on the simulated phase fraction at 7.0 mm from the weld pool centre and figure 7.6b illustrates the effect of changing \( \eta \) on the simulated
Figure 7.5: Initial experimental microstructure in figure 7.5a showing dark pearlite colonies. Simulated microstructures in figures 7.5b, d, and f represent the pearlite as white, the ferrite as lightly shaded, and the austenite as darkly shaded. All phase-field domains are 50 µm x 50 µm. Accompanying carbon concentrations are given in figure 7.5c, e, and g.
phase fraction at 7.5 mm from the centre of the weld pool.

![Graphs showing γ-fraction over time for two positions in the HAZ](image)

Figure 7.6: Comparison of synchrotron measurements at two positions in the HAZ, represented by the vertical lines, with simulations using varied heat source efficiency, $\eta$.

Figure 7.7 shows a compilation of synchrotron data for austenite transformation at a series of positions in the HAZ compared with simulation results using $\eta = 0.93$. The solid lines represent the simulated progression of the austenite fraction in the HAZ during welding, while the vertical data bars represent experimental measurements of the austenite fraction.

![3D graph showing γ-fraction as a function of distance and time](image)

Figure 7.7: Austenite phase-fraction as a function of welding time at various positions from the weld center. Data bars are experimental synchrotron measurements while lines are simulation results.

### 7.6 Discussion

A quantification of the phase transformations at two positions in the HAZ is shown in figure 7.6. These positions (7.0 mm and 7.5 mm from the weld centre) were chosen since
they straddle the completely austenised HAZ and the partially transformed HAZ, and thereby pose a challenging test for the agreement between simulation and experiment. Also represented is the influence of the heat transfer efficiency coefficient, $\eta$, which is the most important unknown in the heat source model. To illustrate the influence of $\eta$ on the thermal model, $\eta$ values of 0.90, 0.93, and 0.96 resulted in peak temperatures next to the weld pool (5.5 mm from the weld centre) of 1652 K, 1703 K, and 1755 K respectively. The thermodynamic driving forces for the transformation and the interface mobility are directly linked to the temperature, which leads the temperature shift due to variance in $\eta$ to have the noticeable influence on phase transformations shown in figure 7.6. Considering the entire HAZ, experimental austenitisation kinetics were best replicated in simulations with $\eta = 0.93$. It is interesting to note the change in simulated austenitisation kinetics after approximately 5 % transformation. This is attributed to the high transformation rate around the carbon-rich pearlite colonies. Once the pearlite is consumed, a distinctly different transformation rate is observed, which coincides with other experimental work on pearlitic steels.\textsuperscript{12}

Figure 7.6 also shows the most crucial shortcomings of the implemented thermal model. The intention was to use a simple, transparent heat source model with as few non-physical fit parameters as possible. However, due to the delayed transformation back to ferrite, especially noticeable in figure 7.6a, it is evident that the calculated thermal cycle stayed above the $A_3$-temperature longer than the experimental material did. In addition, the experimental peak austenite fraction values at 7.5 mm were not attained in the phase-field simulations. In spite of the fact that regions close to the weld (less than 7.0 mm from the weld centre) were above the $A_3$-temperature too long, higher peak temperatures at 7.5 mm from the weld centre would have produced better agreement with the experimentally measured austenite fraction, as seen from the trend of increasing $\eta$ shown in figure 7.6b. This being said, the experimental and simulated peak austenite fraction values at 8.0 mm from the weld centre agreed within 2 %, shown in figure 7.7. This would suggest that the thermal model should have a stronger convective and/or radiative cooling behind the heat source or that the heat source distribution should have wider and shorter dimensions. These adaptations would require a sensitivity analysis beyond the scope of this work.

Final austenite fraction values also warrant mention. It should be recognised that 0 % austenite does not necessarily correspond to 100 % ferrite. Recalling the experimental microstructure in figure 7.3, dark regions of either bainite or pearlitic can be seen. Since these phases were not incorporated into the nucleation model, the simulations calculated approximately 1.5 - 2 % residual austenite, which in reality would transform to bainite or pearlite.

Aside from the discrepancies shown in figure 7.6, the simulated phase fractions shown in figure 7.7 conform well with measured data. Austenitisation kinetics were analysed for the five positions in the HAZ yielding an average deviation of less than 8 %, which included the over-prediction at 6.0 mm and 6.5 mm and the under-prediction at 7.5 mm. When regarding the entire HAZ transformation data, the degree of misfit between experiment and simulation can be put into perspective. Interpolating experimental data shows that the simulation results for 7.5 mm would be well fitted at 7.75 mm. Likewise, the $\pm 0.5$ mm error in experimental positioning of the $\chi$-ray could also be a plausible explanation for the discrepancy. Nevertheless, as a whole, the simulated phase fractions demonstrate very good agreement with the trends in experimental values, both in spatial and temporal aspects.
CHAPTER 7. PHASE TRANSFORMATION: LOW-CARBON STEEL.

7.7 Conclusions

An adaptation of the Goldak double-ellipsoid heat source model has been used to reproduce the temperature distribution in the heat affected zone (HAZ) of autogenous arc welds on AISI1005. Microstructure evolution in the HAZ has been simulated with the phase-field method. Thermodynamic forces for transformation were derived from a linearised phase diagram. To reduce computational costs, pearlite was modelled as a homogeneous phase with an average composition. Local inhomogeneities in composition, such as those resulting from the initial ferrite:pearlite microstructure, were seen to play a role in the developing phases and morphologies. A phase-dependent expression for the mobility of inter-phase interfaces was implemented using the average atomic spacings of each phase as a parameter. The simulated austenitization of a ferrite:pearlite microstructure as well as the transformation to ferrite upon cooling were shown to agree with experimental measurements in spatial and temporal aspects.
References


Chapter 8

Phase Transformation: Dual-Phase Steel

8.1 Introduction

The simulation and experimental validation for the phase transformations during heating and cooling of dual-phase (ferrite and martensite) steel is presented in this chapter. A brief introduction to the physical phenomena occurring during heating and cooling of dual-phase steel is given in section 8.2. The thermal and material model construction is presented in section 8.3. The material model for martensite allows the calculation of driving forces for austenitisation based on thermodynamic data of ferrite and austenite. In the presentation of the material model, details are also given on the sub-model for the implementation of classical nucleation within a phase-field simulation. The modelling and experimental results are presented in section 8.5. This is followed by a discussion of the results in section 8.6.

8.2 Physical Phenomena

Austenite cooled below the $A_3$-temperature will transform to ferrite, which involves the crystallographic rearrangement from a face-centred-cubic (fcc) to a body-centred-cubic (bcc) structure. The bcc arrangement cannot absorb as much carbon as the fcc arrangement. If carbon-rich austenite is cooled too quickly, interstitial carbon cannot diffuse away and the rearrangement to ferrite is hindered. If the undercooling exceeds a critical amount, the austenite will undergo a displacive rearrangement to produce martensite. Martensite is designated as having a body-centred-tetragonal (bct) configuration, which can be viewed as a distorted bcc configuration due to the excess carbon. Heating martensite to moderate temperatures (say 500 K for an hour) will allow the iron atoms to relax into their bcc configuration as the carbon diffuses out to form carbides. Thermodynamic data for martensite is scarce in the literature, which leaves modelling its austenitisation challenging. Therefore, the approach proposed here is to treat martensite thermodynamically as a bcc phase with a carbon super-saturation.
Gibbs free energy curves quantify the free energy of a particular phase as a function of composition for a given temperature, and are well defined for ferrite and austenite. A schematic representation of a Gibbs free energy diagram for the binary iron-carbon system is shown in figure 8.1a and 8.1b. A series of these diagrams at different temperatures forms the basis for the common equilibrium phase diagram.

Figure 8.1a illustrates that below the A1-temperature, a super-saturated ferrite such as one with the martensitic composition c(α') exhibits a driving force for the nucleation of Fe₃C, as indicated by ΔG₀ₐ. However, due to the low diffusivity and interface mobilities at temperatures below A₁, this transformation is neglected in the present model. Approaching the A₁-temperature, diffusivity and mobilities increase and the phase curves shift. Above the A₁-temperature, shown in figure 8.1b, ferrite (c(α)) is in equilibrium with austenite (c(γ)) and martensite that has not decomposed exhibits a thermodynamic driving force for the nucleation of austenite, ΔG₀₉. With a further increase in temperature, the γ-curve will continue to sink, representing the increasing stability of austenite, which results in an increase in the driving force to transform any remaining ferrite and martensite to austenite. By repeated analysis of these curves at increasing temperatures, a function for the increase in driving force for nucleation can be derived. This temperature- and composition-dependent driving force characterizes the nucleation and growth behaviour of austenite in martensite in the presented model.

8.3 Model Construction

8.3.1 Thermal Model

The experimental synchrotron measurements designed to validate the modelling work in this chapter used controlled electrical resistance heating to induce phase transformations,
Figure 8.2: The initial experimental microstructure with light ferrite and dark martensite is shown on the left. The initial simulated microstructure is shown in the middle, with ferrite ($\alpha$) in grey and martensite ($\alpha'$) in white. The scale bar in the simulation domain is 20 $\mu$m. A 3-D microstructure with transverse grains and a solid grain boundary network was used to determine the relation between corner and edge points, seen on the right.

presented in section 8.4. The controlled heating was chosen in order to remove the uncertainty in the thermal field which is often the case in welding experiments. Therefore, thermal boundary conditions for the controlled heating simulations were taken directly from measured temperature data. Since the measured data inherently captures effects of temperature dependent thermal conductivity and latent heat, these effects are implicitly brought into the model.

8.3.2 Material Model

Initialisation

Construction of the simulation requires definition of the computational domain, initial microstructure including phase distribution and initial concentrations in each phase, thermophysical properties of the interfaces, and the thermodynamic interaction between the considered phases. All simulations in the present work were carried out on a two-dimensional 40 $\mu$m by 40 $\mu$m grid with a 0.2 $\mu$m grid spacing. In a previous phase-field investigation, boundary conditions showed an unnatural influence on grain growth if the domain size was too small. The magnitude of this finite size effect was dependent on how the domain size related to the characteristic length of interest, namely grain size when studying grain growth and the diffusion length when studying diffusion controlled transformations. With increasing domain size, the boundary conditions have a decreasing influence on the solution to the point where a further increase in domain size indicates that the final solution has converged. Preliminary investigations showed that a domain larger than 40 $\mu$m by 40 $\mu$m had negligible influence on the calculated phase fraction and that computation time increased quadratically with domain length.

The initial microstructure was based on measured grain sizes and phase fractions from the as-received material, shown in figure 8.2a. Samples were etched with 2% Nital for 3 s.
revealing a light grey ferrite matrix and darker brown martensite under optical microscopy. Approximately 1% retained austenite can be identified as lighter shaded inclusions, often in the bulk of the ferrite grains, but retained austenite was neglected in constructing the initial simulated microstructure. After defining grain sizes, the number of grains and the phases of the respective grains, the initial microstructure was constructed as seen in figure 8.2b, where grey indicates ferrite and white indicates martensite. Although the calculations were performed in two dimensions, important information for the nucleation routine was gained from the initialisation of the three-dimensional microstructure seen in figure 8.2c. This will be further addressed in the presentation of the nucleation routine. In the simulations, the ferrite matrix was given an initial carbon concentration of 3.01 wt%, based on the calculated equilibrium composition at holding temperatures during production of this dual phase steel. The initial phase fraction of α’ was determined using optical micrography and the AnalySIS® software to integrate the area of pixels meeting the desired brightness criterion. Using the average measured phase fraction of 12% α’ in the as-received material and the measured overall composition of 0.09 wt% carbon as constraints, the carbon concentration in the initial α’ was set to 0.70 wt%.

According to the temperature- and phase-dependent interface mobility model developed in section 3.2 of this thesis, the mobility of an interface, $M_{ij}$, can be expressed as

$$M_{ij} = M_0 \cdot \exp \left( \frac{-Q_m}{kT} \right)$$

with

$$M_0 = \frac{d_{ij}^4 \nu_0}{kT},$$

where $Q_m$ is the activation energy for atomic motion and $d_{ij}$ is the average atomic spacing in the two phases (i and j) separated by the interface in question. Table 8.1 summarises the parameters used for the mobility calculations as well as the phase dependent interfacial energies ($\gamma_{ij}$) obtained from the literature where possible. Austenite is indicated by $\gamma$ without subscripts. Interfacial energy and activation energy for martensite ($\alpha'$) were estimated from the published values for ferrite ($\alpha$). Due to the high carbon concentration and resulting strained lattice in $\alpha'$, it is most likely that the energy of an $\alpha : \alpha'$ interface is higher than that of an $\alpha : \alpha$ interface at room temperature. However, due to the high diffusivity of carbon at the temperatures studied here and the concentration gradient across the $\alpha : \alpha'$ interface, the interfacial energy of the $\alpha : \alpha'$ interface is assumed to converge to that of $\alpha : \alpha$ interfaces.

Phases that were considered in the simulations included regular bcc ferrite, an originally super-saturated bcc ferrite mimicking martensite, and austenite. It was assumed that the heating rates and thermal cycle times involved would not give sufficient time for the formation of significant amounts of carbides or pearlite and they were not identified in the final experimental microstructures. The formation of bainite or martensite upon
Table 8.2: Allying elements in wt% (Balance Fe).

| Element | 1.72 | 0.09 | 0.263 | 0.014 | 0.008 | 0.002 |

cooling is not included in the model. The displacive mechanism for the formation of these phases is dependent on the complex stress state and crystallographic orientation, which is not included in the presented work. However, the cooling rate investigated, although significant, was not near the cooling rates of quenching during production and therefore not considered to produce large amounts of martensite.

Thermodynamics

Microstructure simulations were carried out with the multi-phase phase-field code MICRESS, which is based on the work of Steinbach et al. In order to define the thermodynamic interaction between the phases in the phase-field code, a linearised phase diagram was made. Given the alloy composition shown in table 8.2, a pseudo-binary phase diagram was calculated with Thermo-Calc using the TCFE2 database and is shown in light grey in figure 8.3.

Due to the high heating and cooling rates studied, carbon was the only element considered to have appreciable diffusion. Other elements, such as manganese, were assumed to remain in the initial, nominal ratio with the iron atoms throughout the domain, regardless of phase transformations or carbon diffusion. This implies a condition of para-equilibrium, shown by the dark solid lines in figure 8.3. If the distribution of other alloying elements is not homogeneous, this can have ramifications on the size of the two-phase region for localised regions of inhomogeneity. For example, the A3-temperature under para-equilibrium is 1075 K with the alloy composition given in table 7.2, while local A3-temperature is 1090 K if the Mn content in a localised region is 1.0 wt%. However, it is assumed here for simplicity that only carbon has an inhomogeneous distribution in the initial microstructure.

Another important question that is raised when considering martensite is the influence of the stress field on the austenite transformation. The typical 3% expansion and shear due to the formation of martensite create a complex stress state which is difficult to quantify. However, some simplifying assumptions permit a better grasp of the situation. Studies have been performed in which a martensitic island is approximated as a sphere in a ferrite matrix. Bourrel et al. took Hill’s analysis of the plastically deformed ferrite, it was inferred that the stress levels at the ferritic : martensitic interface could reach 300 MPa. Taking this as an extreme case, Thermo-Calc calculations were performed for determining the influence of 300 MPa of compressive stress on the stability of austenite, shown by the dotted line in figure 8.3. Higher pressure should make the fcc austenite more stable as it is a more efficient packing of atoms than the bcc crystal structure. However, the calculations revealed a relatively small effect. Also considering the temperatures reached before austenitisation occurs, temperature dependent mechanical data on ferrite indicates that significant stress relief through thermal softening will negate the compressive stress.
state that exists at room temperature. The implemented linearised phase diagram was therefore a best fit to the bold para-equilibrium lines within the two-phase temperature range, shown in bold grey in figure 8.3.

![Phase Equilibria Diagram](image)

Figure 8.3: Phase equilibria for the considered DP600 alloy. A pseudo-binary iron-carbon equilibrium diagram is given in grey while the dark solid lines represent the phase stability between ferrite and austenite under para-equilibrium conditions at atmospheric pressure. The dotted lines represent para-equilibrium under 300 MPa pressure. The dark grey line indicates the implemented linearisation of para-equilibrium while the average composition is indicated with the vertical line.

**Nucleation**

Incorporating the classical nucleation theory (CNT) in phase-field modelling requires forming a temperature dependent expression for $\Delta G_{ic}$, as discussed in chapter 4. In chapter 4, the nucleation rate was shown to follow

$$
\dot{N} = \sum \beta^* N^j \exp \left( \frac{-\Delta G^{*j}}{kT} \right),
$$

with $z$ as the Zeldovich factor, $\beta^*$ as the frequency factor, $N^j$ as the number of potential nucleation sites, and $\Delta G^{*j}$ as the critical driving force for nucleation. The index $j$ indicates the various types of nucleation sites in a typical multi-crystalline material, namely grain corners, edges and faces. The critical driving force for nucleation was shown to depend on the driving force for transformation and a geometrical factor for the given type of nucleation site, $\Psi^j$. Values for potential face ($\Psi^F = 2.1 \times 10^{-6} \text{ J}^3 \text{ m}^{-6}$), edge ($\Psi^E = 1.3 \times 10^{-6} \text{ J}^3 \text{ m}^{-6}$), and corner ($\Psi^C = 5.0 \times 10^{-6} \text{ J}^3 \text{ m}^{-6}$) nucleation sites were found in the literature. These values were used for nucleation of austenite and ferrite. Using the 1CFe2 database, the driving force for austenite transformation in carbon-enriched
Table 8.3: Nucleation parameters

<table>
<thead>
<tr>
<th></th>
<th>$\alpha \rightarrow \gamma$</th>
<th>$\gamma \rightarrow \alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$ [J m$^{-3}$ K$^{-2}$]</td>
<td>0</td>
<td>1047.83</td>
</tr>
<tr>
<td>$\omega$ [J m$^{-3}$ K$^{-1}$]</td>
<td>100</td>
<td>$-242.27 \cdot 10^4$</td>
</tr>
<tr>
<td>$\chi$ [J m$^{-3}$]</td>
<td>$7.05 \cdot 10^7$</td>
<td>$1.4 \cdot 10^9$</td>
</tr>
<tr>
<td>$N_h^C$ [m$^{-2}$]</td>
<td>$1.88 \cdot 10^9$</td>
<td>$7.50 \cdot 10^9$</td>
</tr>
<tr>
<td>$N_h^E$ [m$^{-2}$]</td>
<td>$1.88 \cdot 10^{10}$</td>
<td>$7.50 \cdot 10^{10}$</td>
</tr>
<tr>
<td>$N_h^F$ [m$^{-2}$]</td>
<td>$1.00 \cdot 10^{11}$</td>
<td>$5.00 \cdot 10^{11}$</td>
</tr>
<tr>
<td>$Q_h$ [kJ mol$^{-1}$]</td>
<td>250 $^{11}$</td>
<td>284 $^{9}$</td>
</tr>
</tbody>
</table>

Ferrite was calculated to grow linearly with temperature. The driving force for ferrite formation in austenite upon cooling followed a quadratic relationship with increasing undercooling. These relationships were described in a general, second-order polynomial form given by

$$
\Delta G_{\text{nc}}(T) = \lambda \, T^2 + \omega \, T + \chi,
$$

(8.3)

with parameters $\lambda$, $\omega$, and $\chi$ defined in table 8.3. Values for $N^j$ were derived from the hosting microstructure. The nucleation site densities in table 8.3 were determined using the procedures for manual summation of the various types of potential nucleation sites as outlined in chapter 4. Values for $Q_h$ for the derivation of $\beta^*$ in equation 4.1 were also found in the literature.$^9,^{11}$ The simplifications in the nucleation routine implemented here compared with the routine presented in chapter 4 is the assumption of a constant average composition of the hosting phase and keeping $N^j$ constant throughout the simulation.

With this information, a unique nucleation rate can be determined for potential corner, edge and face sites in each of the smaller temperature ranges. For corners, for example, the nucleation routine searches the computational domain for grid points which belong to the interface between more than two grains. The time between searches for potential corner nucleation sites, $t_n^C$, is defined by

$$
t_n^C = (N^C)^{-1} = \left( Z \beta N_h^C \exp \left( \frac{-\Delta G_{n,C}}{kT} \right) \right)^{-1}.
$$

(8.4)

If such a grid point is found and it has a thermodynamically favourable composition and temperature, the grid point is switched to the nucleating phase.

The nucleation temperature range of 955 K to 1120 K was discretised into ten temperature regimes. For each temperature regime, a unique nucleation rate was calculated for potential corner, edge, and face nucleation sites for austenite upon heating and for ferrite upon cooling. These calculated rates governed how often MICRESS® could call the nucleation routine for corner, edge, and face nucleation while within a given temperature regime. For corners, the nucleation routine then searched the computational domain with a frequency determined by equation 8.4 for a corner satisfying the thermodynamic requirements for nucleation. If no corner point satisfied the thermodynamic requirements, either due to composition or temperature or the fact that the entire microstructure had already transformed, no nucleus was set. Similar searches for potential edge and face nucleation sites were also performed, each with their own characteristic frequency. A
temporary shielding distance of 5 μm (which lasted an arbitrary 1.5 times as long as the time calculated in equation 8.4) prevented a subsequent nucleus from being set too closely on the same interface. However, this shielding developed naturally with the evolving concentration field. For example, a growing austenite grain withdraws carbon from any neighbouring martensite and also the surrounding ferrite (since the solubility of carbon in ferrite diminishes with temperature). Grid points belonging to an interface going through the carbon-depleted ring of ferrite around the austenite are less favourable for subsequent austenite nucleation than grid points outside of the carbon-depleted ring. This natural passivation of potential nucleation sites is addressed in the discussion. As the simulation temperature evolved and entered a new temperature regime, an updated nucleation rate came into effect. The rates for corner, edge and face nucleation ran simultaneously, leading to an overlap of rates. It should be mentioned that the $N^3$ values in table 8.3 are also set as the maximum number of a given type of nucleus. In this way, the nucleation routine tracks the consumption of potential sites during the transformation.

### 8.4 Physical Experiments

Synchrotron based, *in-situ* x-ray diffraction experiments were carried out using the UNICAT beam line BM-33-C at the Advanced Photon Source (APS) at the Argonne National Laboratory (Argonne, USA). A beam energy of 30 keV from a ring current of 100 mA was used in these experiments. The beam was first passed through a water-cooled Si (111) monochromator and then focussed to a spot size of 1 mm in width and 0.25 mm in height using a dynamically bent Si crystal and collimator slits. The angle of incidence with the sample was 5° which, given the 160 μm absorption length in Fe, provides a penetration depth of 7 μm. The experimental setup is shown schematically in figure 8.4.

![Schematic of the x-ray setup](image)

**Figure 8.4:** Schematic of the x-ray setup used for *in-situ* observations of phase transformations under controlled heating and cooling conditions.

From the calculated phase diagram in figure 8.3, an $A_1$-temperature of 943 K and an $A_3$-temperature of 1076 K for the nominal alloy composition was determined. Based
on these temperatures, two thermal cycles were devised. The first was planned with the intention of inducing considerable, but not complete transformation to austenite before immediate cooling back to room temperature. A peak temperature of 1050 K was chosen for this partial austenitisation cycle and these results are designated PA. The second thermal cycle was designed to induce complete austenitisation before immediate cooling to room temperature. For this purpose, a peak temperature of 1150 K was chosen and resulting measurements are labelled CA. Heating in both cases was done at 20 K s\(^{-1}\) up to 900 K, at 15 K s\(^{-1}\) during the transformation up to the peak temperatures, and cooling at 10 K s\(^{-1}\).

Direct resistance heating of the 100 mm long by 4.75 mm wide by 2 mm thick test coupons was used for rapid heating, while water-cooled grips allow for controlled cooling of the samples. The temperature of the sample was monitored and recorded using type-S (Pt/Pt-10%Rh) thermocouples which were spot welded on the lower face of the sample directly below the x-ray impingement point. The diffracted beams were collected using a CCD detector manufactured by Roper Scientific (A99401, RS/Photometrics) and placed 330 mm behind the sample. This detector uses a 6.1 x 6.1 cm\(^2\) array of 1024 x 1024 pixels on a 60 micron grid to capture the diffraction patterns produced on a scintillating screen, which is connected to the CCD array using a fiber optic bundle. The sampling rate with this detector was 0.33 Hz. An advantage of the 2D detector is that a large number of grains satisfy the diffraction condition for detection than would for a conventional \(θ/2θ\) scan. This allows statistically valid diffraction data to be collected for coarser grained samples. The Debye arcs of the diffracted beam cover a \(d\)-spacing range from approximately 1.1 to 2.4 Å which, for the current experimental design, includes the bcc \{200\}, \{211\}, and \{110\} and the fcc \{220\}, \{200\}, and \{111\} diffraction peaks.

To calibrate the x-ray detector, the room-temperature lattice parameters of the base metal were first measured using a conventional CuK\(_α\) x-ray diffraction system. The Debye arcs were converted into a plot showing diffracted beam intensity as a function of \(d\)-spacing using Fit-2D software.\(^{12, 13}\) This software integrates the diffracted beam intensity for each arc over the entire two-dimensional area, providing the data used to create the diffraction patterns considered in the following analysis.

Figure 8.5a displays a typical diffraction pattern obtained during the heating of a sample to a temperature of 1050 K. Both ferrite and austenite peaks are present in this diffraction pattern. The three ferrite and three austenite peaks present in each diffraction pattern are summarized in table 8.4. It should be noted at this point that diffraction peaks generated by martensite present in the original material cannot be distinguished from the ferrite peaks for this low carbon steel. The peak position, the width, which is defined as the full width at half maximum (FWHM), and the integrated intensity of the peaks in each diffraction pattern were then measured. In order to take into account any variations in the intensity of the synchrotron beam, the intensities of the peaks in each diffraction pattern were normalized with respect to the maximum peak intensity measured in that pattern. A typical diffraction pattern showing the presence of ferrite and austenite phases in a sample during heating to a temperature of 1050 K is shown in figure 8.5b. Each of the peaks is identified with the appropriate phase and corresponding Miller indices. The raw integrated intensity values measured from the peaks present in each diffraction pattern were then converted into relative peak intensities. This conversion was performed
by dividing the raw intensity of each peak by the converting factor $k_o$, given by

$$k_o = \frac{F^2}{V^{1/2}} \ m \ L \ P \ e^{-2M},$$

where $F$ is the structure factor, $V$ is the unit cell volume, $m$ is the multiplicity, $L$ is the Lorentz factor defined by $(\sin \theta \ \sin 2\theta)^{-1}$, $P$ is the polarization factor, and $e^{-2M}$ is the Debye-Waller temperature factor. These factors are discussed in detail in a standard x-ray diffraction reference.\textsuperscript{14} Values for the unit cell volume for each phase, along with the structure factor and multiplicity values for each peak are provided in table 8.4. Structure factor and multiplicity values were calculated using Crystallographica (Oxford Cryosystems, 1999). The atomic spacing, $d$, and the diffraction angle for each peak, $2\theta$, which were observed at 1050 K are also listed in table 8.4. The sum of the converted intensities for all diffracting planes for a given phase divided by the total of all converted intensities provided the instantaneous phase fraction.

Several simplifying assumptions have been made in the conversion of the raw peak intensity values. In particular, the polarization factor was set equal to unity because the synchrotron radiation used in the experiments was, to a good approximation, horizontally polarized. Debye temperatures of austenite and ferrite are the same within the experimental uncertainty, so it is assumed that the temperature factors are the same for each phase, which then cancels out the temperature effects in the conversion of the raw peak intensities. In spite of these assumptions, in other work employing the identical experimental techniques,\textsuperscript{15} the calculated phase fractions deviated only ±1% from metallographic analysis. In the samples studied here, good diffraction peaks were obtained with no indication of texture. The detectability of synchrotron measurements for austenite in initial room temperature measurements was on the order of 1% and lead to a calculated austenite phase percentage of 1.5% and 1.8% in the PA and CA samples respectively.
Table 8.4: Summary of peaks observed in X-ray diffraction patterns.

<table>
<thead>
<tr>
<th></th>
<th>V [Å³]</th>
<th>hkl</th>
<th>d [Å]</th>
<th>2θ</th>
<th>F²</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenite (fcc)</td>
<td>43.76</td>
<td>111</td>
<td>2.126</td>
<td>11.6597</td>
<td>5296.70</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>1.841</td>
<td>13.4712</td>
<td>4549.25</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>1.302</td>
<td>19.0956</td>
<td>2772.43</td>
<td>12</td>
</tr>
<tr>
<td>Ferrite (bcc)</td>
<td>23.55</td>
<td>110</td>
<td>2.036</td>
<td>11.7037</td>
<td>1319.82</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>1.440</td>
<td>16.5805</td>
<td>868.657</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>1.175</td>
<td>20.3428</td>
<td>624.477</td>
<td>24</td>
</tr>
</tbody>
</table>

was within ±1% of the 1% austenite present in metallographic analysis of the as-received material (see figure 8.2a).

8.5 Results

The effect of implementing the classical nucleation theory in the phase field model can be seen when tracking the rate with which new austenite grains were added to the microstructure upon heating and the rate with which new ferrite grains were introduced upon cooling. Figure 8.6a shows the simulated number of austenite grains as a function of time during heating. By considering the slope, a distinct increase in nucleation rate with increasing temperature is observed. The decrease in the number of austenite grains after 45 s indicates grain growth and accompanying grain agglomeration in the fully austenitic microstructure. Figure 8.6b shows the increase in the number of ferrite grains as the fully austenitised microstructure cools below the A₃-temperature. Although the driving force for transformation to ferrite continues to grow with decreasing temperature, the atomic mobility reduction is stronger.

The activation energy for interface mobility is taken as the activation energy for bulk self-diffusion minus the activation energy for vacancy creation. The activation energy for Fe diffusion in ferrite is 260 kJ mol⁻¹ and the activation energy for vacancy creation can be estimated as 100 kJ mol⁻¹. This leads to a theoretical value of $Q_m$ of 160 kJ mol⁻¹. Preliminary calculations were made using values of $Q_m$ ranging from 155 kJ mol⁻¹ to 165 kJ mol⁻¹, as shown in figure 8.7. The best agreement with for austenitisation kinetics was achieved with $Q_m = 160$ kJ mol⁻¹ and was implemented as such for the rest of this work.

The progression of the measured and simulated phase fraction with time during the PA-cycle, as well as the measured temperature evolution, is given in figure 8.8. Measured temperature data was used as the thermal boundary condition for the simulations and, due to the small domain being investigated, thermal gradients were considered negligible. The peak simulated austenite fraction was 38.2% while the measured peak austenite fraction was 31.0%. As mentioned in section 8.4, the error in measured phase fractions is expected to be on the order of ±1%, which is too small for the scale used in figure 8.8 (or figure 8.9). Upon cooling after approximately 50 seconds, the experimental austenite exhibited
Figure 8.6: Simulated nucleation rates during heating of the completely austenitised sample. The solid line indicates the temperature.

Figure 8.7: Sensitivity of phase transformation kinetics to a range of $Q_m$ values.

a noticeably higher stability than the simulated austenite. After 65 seconds, the simulated and measured austenite fractions converged. The simulated austenite fraction after 150 s was 6.7%, compared to the experimental value of 7.2%.

The experimental and simulated progression of phase fraction with time for the CA thermal cycle is given in figure 8.9. The simulated $\alpha + \alpha' \rightarrow \gamma$ transformation reflects the measured austenitisation. As with the PA sample, the initial stages of the $\gamma \rightarrow \alpha$ transformation were slower in experiment than in the simulation. After 70 seconds, the simulation and measured austenite values coincided. The calculated retained austenite value was 10.3% after 150 s, compared to the measured value of 9.8%.

Figure 8.10 displays the simulated evolution of the phases and carbon concentration profile during heating at 15 K s$^{-1}$ to the intercritical temperature of 1050 K and cooling at 10 K s$^{-1}$ to room temperature, the PA-cycle. At 44 s, shown in figure 8.10a and d, the calculated austenite levels approach 20% and significant concentration gradients within the austenite can be seen. Ferrite, having the lowest carbon solubility, is associated
Figure 8.8: Measured and simulation phase fraction as a function of time during the PA thermal cycle. Temperature is read off the right-hand axis.

Figure 8.9: Measured and simulation phase fraction as a function of time during the CA thermal cycle. Temperature is plotted according to the right-hand axis.
Figure 8.10: Simulation results of phase and carbon concentration evolution during the PA-cycle. In figures a, b, and c, the ferrite matrix is shown in light grey (indicated with \( \alpha \) in figure a), the martensite in white, and the austenite (indicated with \( \gamma \) in figure a) is represented with dark grey. Figures d, e, and f show the corresponding carbon concentration distribution with the scale in wt%.

with the darkest regions in the concentration map. Figure 8.10b and e show the phase and concentration distribution at the maximum austenite fraction of 38%. Although the carbon within each austenite grain has homogenised considerably, noticeable concentration variation exists between austenite grains. The concentration distribution after 100 s in figure 8.10f illustrates the effect of the growing ferrite rejecting carbon and the consequent enrichment of carbon in the austenite. This figure also shows the effect of lower diffusivity of carbon in austenite, evident by the persistent concentration gradients in the large austenitic regions.

The simulated evolution of the phases and carbon concentration profile during the CA-cycle is shown in figure 8.11. Austenite grains in figure 8.11a are seen to have a noticeable concentration variation in figure 8.11d, depending on how much martensite was locally transformed. At 46.1 s, figure 8.11b and c, the microstructure is completely austenitised but carbon concentration gradients remain. Upon further cooling, growing ferrite rejects
carbon and produces a microstructure after 100 s of a ferrite matrix with carbon enriched retained austenite, seen in figure 8.11c. The narrow regions of retained austenite also exhibit noticeable concentration gradients, as can be seen in figure 8.11f.

After 150 s, both simulated microstructures exhibited no noticeable change. By this time, the temperature in the PA-cycle had dropped to 493 K while the CA-cycle has dropped to 543 K. The final simulated microstructure of the PA-cycle is compared to the final experimental microstructure in figure 8.12a and c while the simulated and experimental microstructure produced by the CA-cycle are shown in figure 8.12b and d. For the PA-cycle, the average simulated ferrite grain size increased from 6.8 μm to 7.9 μm while the experimental ferrite grain size increased from 7.2 μm to 9.7 μm. The simulated microstructure resulting from the CA-cycle produced a final ferrite grain size of 9.6 μm while the experimental ferrite grain size was 13.5 μm.
Figure 8.12: Final microstructures after simulated and experimental thermal cycles. Partially austenitised and cooled samples are shown in figures a and c, while fully austenitised and cooled samples are shown in figure b and d. Dark phases in figures a and b represent retained austenite, which agree within 1.5% of measured retained austenite values in the microstructures shown in figures c and d.
8.6 Discussion

The present study shows that the proposed adaptations to modelling martensite and incorporating classical nucleation theory into the phase-field method are capable of representing the austenitisation of a dual-phase microstructure and the reversion to ferrite upon cooling. Nevertheless, a few general comments to the simplifications and assumptions in the model are necessary. The assumptions having the largest impact are the applicability of 2-D calculations to 3-D experimental results, the linearisation of the phase diagrams, and the initial homogeneous distribution of other alloying elements. At this point, although 3-D simulations have been investigated,\textsuperscript{17} large scale 3-D calculations are not yet computationally feasible. In 2-D, it is necessary to assume that the differences between boundary conditions for diffusion and grain impingement in 2-D and 3-D are small. If these discrepancies were significant, they would be visible in the final stages of austenitisation (around 50 s in figure 8.9) and during carbon-enrichment of the austenite in final stages of cooling (around 100 s in figure 8.8 and 8.9). The simulations vary somewhat from measured values at these points, but remain within the 2.3% spread in experimentally measured austenite fractions during replicative measurements. Therefore, this first assumption appears justified.

The linearised phase diagram provides a numerically efficient manner of describing relative phase stability. In this study, carbon distribution and diffusion are considered to be the sole compositional factor for phase transformation. As can be seen in figure 8.3, the implemented linearisation would calculate austenite just above the A1-temperature as having a lower carbon concentration than predicted by the TCFe2 database. However, since diffusivity of elements increases exponentially with temperature and considering the PA and CA thermal cycle, it is more crucial to have strong agreement between the linearisation and database values for the upper portion of the two-phase region. The current model is limited to linearised phase diagrams. Future research will determine if this has led to significant error.

The assumption likely to have the most negative impact on agreement between simulation and experiment is that of the homogeneous distribution of manganese in the initial microstructure. The production of dual-phase steels involves an intercritical isothermal hold to allow the desired $\alpha : \gamma$ ratio to develop, followed by a quench to convert the austenite to martensite. This intercritical hold is generally in the order of minutes and thus not long enough to homogenise the inhomogeneous Mn distribution inherent in the cast microstructure. Austenite has a higher affinity for manganese than ferrite and will therefore form in Mn-rich regions. At 975 K, approximately 25 K above the alloy A1-temperature, ThermoCalc\textsuperscript{5,19} calculations show that the equilibrium content of Mn in austenite is 3.6 wt% while the ferrite contains only 0.8 wt% Mn. Manganese has a diffusivity an order of magnitude lower than carbon and is also known to stabilise austenite.\textsuperscript{5} The martensite that results from the quenched austenite is therefore richer in Mn than the surrounding ferrite matrix. This also means that upon reheating, the austenite transformed from martensite has a higher manganese content than the average composition and is therefore stable to lower temperatures than predicted by the shown para-equilibrium state (see figure 8.3). For the fully austenitised sample, this error is quite small since the average manganese content of the austenite is in fact the nominal manganese content. The fully austenitised microstructure has grains with higher than nominal manganese content and grains with lower than nominal manganese content. However, the deviation between simulation and
CHAPTER 8. PHASE TRANSFORMATION: DUAL-PHASE STEEL

experiment is more prominent for the partially austenitised sample, as seen between 50 and 70 seconds in figure 8.8. Due to preferential austenitisation of the martensite, the majority of the austenite that forms in this sample has a higher than nominal manganese content and therefore exhibits a stability to lower temperatures than the simulated austenite. Simulations that consider a non-homogeneous distribution of manganese in the initial microstructure are part of ongoing research. MICRESS® has the capabilities to calculate multiple diffusion fields and influence of Mn on phase stability can also be calculated, but the sensitivity of the solution to numerical parameters such as time step and grid spacing needs to be carefully investigated.

The developed nucleation routine has several important features. Firstly, considerations for super-heating are inherent due to the temperature-dependent nucleation rate seen in figure 8.6. Lower heating rates, due to the longer times spent in the first temperature ranges, would allow austenite nucleation at lower temperatures while higher heating rates would increase the super-heating. Another important feature is the explicit tracking of individual potential nucleation sites. The microstructure is defined as having \( \sum N \) potential sites before transformation. This represents the maximum number of nuclei if the heating (or cooling) rate was large enough that all nucleation took place before diffusion and phase growth could disturb any neighbouring potential sites. However, as the transformation proceeds and the microstructure evolves, potential sites can be consumed or passivated. Potential nucleation site consumption occurs, for example, after complete austenitisation. Even if not all of the \( \sum N \) nuclei have been set, no further austenite nucleation will occur if the entire microstructure is austenite. This was demonstrated in the PA-cycle where only 111 austenite nuclei out of 193 potential nuclei were set. This behaviour was observed for ferrite nucleation as well. A potential site become passivated if it evolves microstructure and associated concentration field, that particular site no longer has a composition that makes nucleation thermodynamically possible. The critical mechanisms are the moving phase fronts and diffusion, and it is observed, for example, during the ferrite growth and carbon enrichment of the retained austenite. Many nucleation models attempt to reduce the nucleation rate during transformation with the factor \( (1 - f_x) \), where \( f_x \) is the phase fraction of the nucleating phase. However, such an approach only includes the influence of site consumption and not of site passivation, whereas the present model includes both phenomena. Finally, it should be noted that the location of nuclei was not artificially pre-determined. For example, the probability of corner nucleation was equal among all potential corner nucleation sites, as long as the potential site was not passivated. There was also equal probability among the potential edge and face nucleation sites. The supply of carbon determined growth kinetics after nucleation, but the initial position was not manipulated. It is the authors’ opinion that this is a more fitting representation of the real nucleation phenomenon than confining nucleation only to martensitic islands. The difference in austenitisation rates with a ferritic:martensitic microstructure is related to the diffusion length of carbon to the growing austenite. At an \( \alpha : \alpha' \) interface, this distance is much shorter than the distance to the bulk of a ferrite grain.

There are other important features of the simulation results. As already mentioned, synchrotron measurements did not distinguish between ferrite and martensite due to the low carbon content of this steel. The advantage of the simulation is that this information is readily available, shown in both figure 8.8 and 8.9. Not only are multiple phase fractions easily discernable, but the composition of phases and composition gradients within a
given phase are standard output. This is important in order to predict how the produced phases will react to following thermal or thermal-mechanical treatments. High carbon concentration gradients within retained austenite could, for example, lead to a dilution of the transformation induced plasticity (TRIP) effect. Distinct concentration gradients can be seen in the retained austenite in figure 8.10f and even larger gradients are observed in figure 8.11f. Finally, although the ferrite grain size in the final microstructures, shown in figure 8.12 had some discrepancies, there are important qualitative similarities. In both simulation and experiment, the CA-cycle led to larger ferrite grains than the PA-cycle. The allotriomorphic distribution of the carbon-rich phases in the simulated PA-cycle agreed with the distribution of carbon-rich phases in the experimental PA sample. The carbon-rich phases in the experimental CA sample were both at grain boundaries and captured within the large ferrite grains, which was also reflected by the simulation results. Correct prediction of these morphologies is important in determining mechanical properties of the final material.

8.7 Conclusions

Nucleation and growth of phases during two heating and cooling cycles of dual-phase (ferrite : martensite) steel was simulated with the phase-field method. Initial microstructures for the simulations were based on experimental micrographs. Critical parameters for the nucleation model were gathered from 3D constructions of the microstructure and adapted for the 2D simulations. Martensite in the starting microstructure was modelled as ferrite with a carbon super-saturation. A phase-dependent model for mobility of interphase interfaces was implemented and the activation energy for this mobility was found to follow theoretical expectations. The implemented nucleation routine produced simulated temperature-dependent nucleation rates for both austenite and ferrite. Simulated results were validated by in-situ synchrotron-based x-ray diffraction experiments. Measurements confirmed the simulated austenitization kinetics. The deviation between simulated and experimental austenite fractions upon cooling was attributed to the inhomogeneous distribution of manganese, which was not accounted for in the simulations. Final measured austenite fractions for both thermal cycles was predicted by the simulations within the uncertainty of the experimental technique.
References


REFERENCES


Part IV

Closing
Chapter 9

General Conclusions

**Dual-Mesh Strategy** The coupling of phase-field modelling to larger scale finite element models has been shown to make detailed microstructure simulations over macroscopic dimensions feasible (see chapter 5, 6, 7, and 8). This opens many doors into more detailed analysis of larger structures.

**Physically-based Material Modelling** Phase-field modelling has been shown to be a versatile and capable tool for simulating a range of materials under a wide range of conditions, provided that the correct physical-basis is incorporated into the material model. This thesis has presented material models for ferrite and austenite based on standard thermodynamic databases and literature values for interfacial energies. Models have also been presented for pearlite and martensite. To reduce computational cost, pearlite has been approximated as a homogeneous phase having the same composition as the alternating lamella of ferrite and cementite in real pearlite, as presented in chapter 7. The driving force for transformation between pearlite and ferrite and pearlite and austenite has therefore also been averaged for a homogeneous composition. Although the pearlite phase fraction was not explicitly measured experimentally, the simulated ferrite-pearlite base material transformed to austenite with kinetics and maximum levels which matched the synchrotron measurements. The material model for martensite, developed in chapter 8, was based on the close relation in crystal structure between ferrite (bcc) and martensite (bct). Treating martensite as ferrite with a super-saturation in carbon allows the derivation of driving forces for austenisation based on established thermodynamic data for ferrite and austenite. These transformation kinetics were validated by synchrotron measurements.

If material models are developed based on physical principles and have incorporated the correct thermophysical data, these models can demonstrate a wide range of applicability (from conventional heat treatments to welding) and thereby deepen understanding of material response to arbitrary processing conditions.

**Interface Mobility Model** A general, temperature-dependent interface mobility model for single-phase microstructures was developed in section 3.2 of this thesis. The model is based on established thermophysical material properties and literature values.
for atomic lattice spacings. The model has a general construction and is not restricted to any given set of material processing conditions. The interface mobility model was implemented in an existing phase-field code and validated for AISI316L austenitic stainless steel subjected to various conventional heat treatments, welding, and combinations of heat treatments and welding (see chapter 6). The conventional heat treatments lasted more than $10^4$ seconds while the welding thermal cycle was on the order of seconds. The calculated interface kinetics predicted grain sizes within the experimentally measured range of grain sizes for the wide range of processing times and temperatures ranging from room temperature to more than 1700 K. This temperature-dependent interface mobility model was expanded to include phase-dependent properties in section 3.4 by taking the atomic spacings on both sides of the interface into account. In chapter 7, the phase-dependent interface model was used to calculate the microstructure evolution during the welding of AISI1005 (a low carbon steel) in which interfaces between ferrite, pearlite, and austenite were simulated. In chapter 8, interfaces between ferrite, ferrite super-saturated with carbon so as to mimic martensite, and austenite were simulated during controlled heating and cooling experiments. The presented interface mobility model exhibited the ability to capture microstructure evolution for a wide range of process conditions.

The temperature-dependence in the model is not only crucial, but has also been shown to be an appropriate dependence for the wide range of temperatures that a material is subjected to during welding. The mobility model was also validated by the range of time scales in the various physical experiments. The activation energy proposed as the activation energy for bulk diffusion minus the activation energy for vacancy creation has proven to be fitting. The adaptations for interfaces between various phases has demonstrated its applicability. The interface mobility model played a central role in calculating the microstructure evolution in all cases studied in this thesis.

**Nucleation in Phase-Field Modelling** Nucleation in phase-field modelling has been modified to incorporate the physically-based concepts of the classical nucleation theory in chapter 4. The various classes of nuclei observed in typical polycrystalline material have been treated and the thermodynamic balance between interfacial free energy and chemical free energy has been considered. Parameters for the calculation of the nucleation rates are gleaned from the literature ($\gamma$, $\beta^*$, $\Psi^*$) or are extracted directly from simulated microstructures ($N^*$). The entire nucleation temperature range is discretised into smaller temperature regimes in which a calculated average nucleation rate for each type of nucleation site governs the phase-field nucleation routine. In section 4.3, this approach was validated against detailed synchrotron measurements in the literature. Both simulated nucleation rates and transformation kinetics agreed with experimental findings. In chapter 7, an earlier version of this nucleation model was implemented in simulating nucleation during welding. In chapter 8, the final version of the nucleation model was implemented in simulating nucleation during controlled heating and cooling.

The method can be improved by considering the change in driving force for transformation which results from the evolving composition in the hosting phase during transformation. However, the data flow in the current version of the phase-field code needs to be modified before this can be implemented. Nevertheless, in its current form, the nucleation model provides an established theoretical and physical underpinning to the simulation of nucleation using the phase-field method.
Summary

Materials science along with improved control of process conditions during manufacturing has enabled the production of metal alloys with desired properties (such as yield strength, formability, or hardness) designed for specific applications. Many of these materials owe their properties to their carefully designed microstructure where grain size, phase fraction, phase distribution, and other microstructural features play an important role. These carefully designed materials are often formed and/or joined before being delivered to the end-consumer. Welding, the most important joining process, destroys the microstructure in the fusion zone, returning it to an as-cast state, and drastically alters the microstructure in the heat affected zone (HAZ) next to the fusion zone.

As reviewed in chapter 2 of this thesis, many welding- and material-models have been developed in the past. Some of the models have furthered the understanding of the thermal conditions which the material is subjected during welding while other models provide insight into how the material responds to these thermal conditions at a microstructural level. Both the thermal and microstructure models reviewed cover various levels of detail. However, there is a gap in the literature when considering models which incorporate sufficient detail for microstructure analysis while still being computationally feasible for simulations of an entire weld. In this thesis, the coupling of existing thermal models with new material models is presented with the aim of improving the understanding of the mechanisms responsible for the evolution of the microstructure in the HAZ. These models are executed with a method enabling the simulations on the scale of entire welds in a computationally feasible manner.

Microstructures are defined to a large extent by interfaces and phases. The mobility of the interfaces, $M$, and the driving force for interface motion, $F$, are inherently coupled by the classical expression for the interface velocity, namely $v_{int} = MF$. The driving force can stem from interfacial energy, from stored strain energy, from a difference in phase stability, or a combination of all three. Theory on interface mobility and thermodynamic driving forces for transformations are presented in chapter 3 along with accompanying implementations with the phase-field method. A sub-model for the interface mobility is developed which uses the average atomic spacing, a characteristic frequency of the material, and an activation energy. The activation energy is proposed to be equivalent to the activation energy for self-diffusion minus the activation energy for vacancy creation. This is followed by an investigation into the thermodynamic driving force behind interface motion and how this can be incorporated in the phase-field method. The chapter is concluded with examples showing both diffusion and interface mobility as the controlling factors in interface motion.
Nucleation is the process by which a new phase is introduced into a microstructure and is central to describing microstructure evolution in welded material. The classical, physically-based theory for nucleation is reviewed in chapter 4. The phase-field equations do not explicitly incorporate nucleation, but it can be inserted between time steps of phase-field simulations in the numerical setting. Earlier nucleation routines in the literature have received criticism for their assumptions such as site saturation nucleation or constant nucleation rate. In the second part of chapter 4, a new strategy for the incorporation of the classical nucleation theory in phase-field simulations is presented. This nucleation routine is implemented in a simulation of the continuous cooling of C35, a medium-carbon steel. These simulations are validated by recent experimental work in the literature which provides direct observation of the nucleation phenomenon. The simulated nucleation density under the assumption of site saturation is 1500% larger than experimentally measured values while the simulated nucleation density resulting from the new routine is 17% larger than the experimental nucleation density.

Chapter 5 introduces a method by which microstructure detail can be calculated over macroscopic distances in a semi-continuous manner. Phase-field domains are placed inside larger finite elements. The finite element mesh calculates the thermal history and provides this as a boundary condition to the resident phase-field domain. This approach is called the dual-mesh strategy. With the dual-mesh strategy, only a fraction of the welded microstructure is explicitly simulated, leading to significant computational savings. Another approach is presented to incorporate the microstructure evolution results of the dual-mesh into thermal-mechanical simulations.

Chapters 6 to 8 present practical implementations of the theory and methods developed in chapters 3 to 5. Grain growth and recrystallization of AISI316L are analysed in chapter 6. As an austenitic stainless steel, AISI316L is an ideal medium to validate the interface mobility model without the complications of phase-transformations. The interface mobility model was validated on the time scale of welding (seconds) as well as conventional heat treatments (hours). The activation energy for the interface mobility was shown to be 197.5 kJ mol$^{-1}$, which only 2.5 kJ mol$^{-1}$ below the theoretically predicted value. Thermal profiles of welding were simulated using an adaptation of the Goldak double-ellipsoid heat source model. The dual-mesh strategy was then implemented to simulate the microstructure evolution at a series of distances from the fusion zone. Recrystallization proved to play an important role in the development of the microstructure and was also simulated. The short duration of the welding thermal cycle was useful in determining the recrystallization nucleation density, since grain coalescence had negligible time to develop.

Phase transformations during welding were simulated in chapter 7. Recent synchrotron-based x-ray diffraction experiments in the literature provided invaluable in-situ, time-resolved phase fraction data during the welding of AISI1005, a low-carbon manganese steel. In these simulations, an adapted Goldak double-ellipsoid heat flux distribution was also used to emulate the welding arc. The initial microstructure was a ferrite matrix with small colonies of pearlite. Values for the initial grain size and initial phase fractions for the simulations were taken from the experimental micrographs. Pearlite was modelled as a homogeneous phase to avoid the computational cost of simulating the individual ferrite and cementite lamellae. The interface mobility model was applied to the multiple phase setting with the atomic spacing being the average atomic spacing of the phases separated by the interface. Local fluctuations in composition due to the initial phase distribution
were seen to have an influence on the location of austenite nucleation upon heating. A predecessor to the nucleation routine presented in chapter 4 was implemented with important parameters gained from the experimental material. Simulated phase fractions were shown to agree with the experimental findings in both spatial and temporal aspects.

The nucleation and growth of phases during the controlled heating and cooling of a dual-phase (ferrite-martensite) steel were investigated in chapter 8. The initial grain size and phase distribution for the simulations were gathered from the experimental material. Martensite was modelled as ferrite with a carbon super-saturation. This assumption founded the relationships for calculating the driving forces for the austenitization of the martensite. The interface mobility was modelled with the theoretical activation energy and atomic spacing. The nucleation routine produced temperature-dependent nucleation rates for austenite upon heating and ferrite upon cooling. The simulated phase fractions were validated by in-situ synchrotron-based x-ray diffraction experiments. The measured austenitization rates for two different thermal cycles confirmed the simulation results. Experimental retained austenite fractions after cooling were within 1% of the simulated values, a difference which was smaller than the experimental uncertainty.

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The results gained from the implementation of the developed material models are promising in several aspects. The four examples of experimental validation show that the physical-basis for the material models presented in thesis has a general applicability. The attention paid to mechanisms of interface mobility and nucleation has played a central role in this success. The road to complete thermal-mechanical simulation of welded material at the microstructural level still has many untravelled miles. The coupling of microstructure detail to mechanical properties requires experimental or theoretically derived phase-dependent mechanical data. Many other aspects, such as the influence of local stress states on nucleation and non-isotropic mechanical properties also require investigation. Optimization of alloy composition and/or process conditions performed with the methods and models presented here can also offer many possibilities. Therefore, this work can be regarded as a building block for further material science research into the material response to welding.
Samenvatting

Materiaalwetenschappen heeft, samen met een verbeterde beheersing van procescondities tijdens productie, het mogelijk gemaakt om metaallegeringen met gewenste eigenschappen (zoals treksterkte, vormbaarheid, of hardheid) te produceren. Veel van deze materialen hebben hun eigenschappen te danken aan hun nauwkeurig ontworpen microstructuur, waar korrelgrootte, fasenfractie, fasenverdeling en andere microstructurele kenmerken een belangrijke rol spelen. Deze nauwkeurig ontworpen materialen worden vaak gevormd en/of samengevoegd voordat ze aan de eindconsumptie worden geleverd. Lassen, het belangrijkste verbindingenproces, vernietigt de microstructuur in de laszone, waardoor het teruggaat naar de gezogen staat en op een drastische wijze de eigenschappen van de warmtebeïnvloede zone (HAZ) naast de las verandert.

Zoals beschreven in de literatuurstudie in hoofdstuk 2 van dit proefschrift, zijn er in het verleden vele las- en materiaalmodellen ontwikkeld. Een deel van deze modellen is gericht op een beter inzicht in de thermische condities waaraan een materiaal wordt blootgesteld tijdens lassen. Andere modellen bestuderen hoe het materiaal reageert op deze thermische condities op microstructureel niveau. Zowel de thermische als de microstructuurmodellen besproken in hoofdstuk 2, beschrijven verschillende detailniveaus. Er bestaat echter een gat in de literatuur wanneer men modellen in beschouwing neemt die voldoende detail beschrijven voor microstructuuranalyse en tegelijkertijd rekenkundig haalbaar zijn op de schaal van een gehele las. In dit proefschrift wordt een koppeling gepresenteerd tussen bestaande thermische modellen en nieuwe materiaalmodellen die het inzicht verbeteren in mechanismen die verantwoordelijk zijn voor de evolutie van microstructuur in de warmtebeïnvloede zone. Deze modellen worden toegepast op een zodanige manier dat simulaties op schaal van een typische las rekenkundig mogelijk worden gemaakt.

Microstructuren worden in grote mate bepaald door hun grensvlakken en fasen. De mobiliteit van deze grensvlakken, $M$, en een thermodynamische drijvende kracht, $F$, zijn gekoppeld door de klassieke uitdrukking voor de snelheid van een grensvlak, namelijk $v_{\text{int}} = MF$. De thermodynamische drijvende kracht kan komen van grensvlakkenergie, opgeslagen rekenenergie, faseinstabiliteit, of een combinatie van die drie. Theorie van grensvlakmobilité en thermodynamische drijvende krachten samen met een implementatie hiervan in de fasen-veidmethode zijn gepresenteerd in hoofdstuk 3. Een sub-model voor de grensvlakmobilité is ontwikkeld waarbij de gemiddelde tomaire afstand, een karakteristieke frequentie van het materiaal, en een activeringsenergie worden gebruikt. Deze activeringsenergie is voorgesteld als equivalent aan de activeringsenergie voor zelfdiffusie min de activeringsenergie voor het creëren van vacatures. Vervolgens zijn de thermodynamische drijvende kracht achter de beweging van het grensvlak en de implementatie.
hiervan in fasenveld bestudeerd. Dit hoofdstuk wordt afgesloten met voorbeelden waar zowel diffusie als grensvlakmobieliteit de grensvlakbeweging bepalen.

Nucleatie is het proces waarbij een nieuwe fase wordt geïntroduceerd in een microstructuur en staat centraal in de beschrijving van microstructuurverandering in gelast materiaal. De klassieke, fysisch gebaseerde theorie voor nucleatie is besproken in hoofdstuk 3. De fasenveldvergelijkingen kunnen nucleatie niet beschrijven, maar nucleatie kan worden toegevoegd tussen tijdstappen van een fasenveldsimulatie in een numerieke omgeving. Eerder voorgestelde nucleatioroutines in de literatuur zijn bekritiseerd om aannamen zoals site satutatie nucleatie of constante nucleatie-snelheid. In het tweede deel van hoofdstuk 4 is een nieuwe strategie voor de implementatie van klassieke nucleatietheorie in fasenveldsimulaties gepresenteerd. Deze nucleatioroutine is geïmplementeerd in de simulatie van continu-alkoelen van C35, een middeldikoolstofstaal. Deze simulaties worden gevalideerd door recent experimenteel werk beschreven in de literatuur dat een direct inzicht geeft op nucleatie. De gesimuleerde nucleatiedichtheid, onder de aanname van site satutatie, is 1500% groter dan experimenteel gemeten waarden, terwijl de simulatiedichtheid van de nieuwe routine slechts 17% groter is dan de experimentele dichtheid.

Hoofdstuk 5 introduceert een methode waarmee microstructurendetail berekend kan worden over macroscopische afstanden op een semi-continue manier. Fasenvelddomen zijn geplaatst binnen een groter eindig element. De eindige element mesh berekent de thermische geschiedenis en geeft dit als een randvoorwaarde aan zijn lasenvelddomein. Deze aanpak wordt twee-mesh strategie genoemd. Met deze twee-mesh strategie wordt alleen een fractie van het gelaste microstructuur gesimuleerd, wat een aanzienlijk besparing in rekentijd oplevert en toch voldoende relevante informatie levert om de verandering van de microstructuur te visualiseren. Een andere aanpak is gepresenteerd om deze berekende microstructurenrevolutie in een thermisch-mechanische simulatie te incorporeren.

Hoofdstukken 6 tot en met 8 presenteren praktische implementaties van de theorie en methoden ontwikkeld in hoofdstukken 3 tot en met 5. Korrelgroei en rekristallisatie van AISI316L zijn geanalyseerd in hoofdstuk 6. Als een austenitisch roestvaststaal, is AISI316L een ideaal materiaal om de grensvlakmobieliteitmodel te valideren zonder de complicaties van fasentransformaties. Het grensvlakmobieliteitmodel was gevalideerd op zowel tijdschalen van lassen (seconden) als tijdschalen van conventionele warmtebehandelingen (uren). De activieringsenergie van grensvlakmobieliteit bleek 197.5 kJ mol⁻¹ te zijn, wat 2.5 kJ mol⁻¹ af ligt van de theoretische waarde. Thermische profielen van lassen zijn gesimuleerd met gebruik van een aangepast Goldak dubbel-ellipsoïde warmtebronnemodel. Vervolgens was de twee-mesh strategie gememoriseerd om de microstructurenrevoeltie te simuleren op verschillende afstanden van de las. Rekristallisatie bleek een belangrijke rol te spelen in de ontwikkeling van de microstructuur en was daarom ook gesimuleerd. De korte duur van de thermische cyclus van het lassen bleek handig te zijn in het bepalen van de rekristallisatienucleatiedichtheid, omdat er onvoldoende tijd is voor korrelcoalescentie om plaats te vinden.

Fasentransformaties tijdens het lassen zijn beschreven in hoofdstuk 7. Recente synchrotron-gebaseerde Röntgendiffractiemetingen in de literatuur geven waardevolle in-situ time-resolved fasenfractie data tijdens het lassen van AISI1005, een laagkoolstofman- gaastaal. In deze simulaties was ook een aangepaste Goldak dubbel-ellipsoïde warmte-fluxverdeling gebruikt om de losboog te simuleren. De oorspronkelijke structuur was een ferrietmatrix met kleine kolonies van perliet. De waarden voor de initiële korrelgrootte en lasenfracties zijn overgenomen van micrographs van experimenteel materiaal. Perliet was
gemodelleerd als een homogene fase om de hoogte van de rekenkosten van het simuleren van individuele ferriet en cementietlamellen te beperken. Het grensvlakmobilitiemodel werd toegepast in de meerfasenomgeving door de gemiddelde atomaire afstand tussen de fasen aan beide zijden van het grensvlak te gebruiken. Locale fluctuaties in de samenstelling vanwege initiële fasenverdelingen hadden een invloed op de locatie van austeniet-nucleatie tijdens het opwarmen. Een voorganger van de nucleatietaferein in hoofdstuk 4 was gemanipuleerd met belangrijke parameters genomen van het experimentele materiaal. Gesimuleerde fasenfracties kwamen overeen met experimentele metingen in zowel ruimtelijke als in tijdafhankelijke aspecten.

De nucleatie en groei van fasen tijdens gecontroleerd opwarmen en afkoelen van een twee-fasenstaal (ferriet:martensiet) werden bestudeerd in hoofdstuk 8. De initiële korrelgrootte en fasenverdeling voor de simulaties werden genomen van experimenteel materiaal. Martensiet was gemodelleerd als een ferriet overzadigd met koolstof. Deze aan- name was de basis voor de verhoudingen om de drijvende kracht voor austenietvorming te berekenen. De grensvlakmobilitiet was gemodelleerd met de theoretische activeringsenergie en atomaire afstand. De nucleatietaferein leverde temperatuurafhankelijke nucleatiesnelheden voor zowel austeniet tijdens opwarmen als voor ferriet tijdens afkoelen. Deze gesimuleerde fasenfracties waren gevalidereerd door in-situ synchrotron-gebaseerde Röntgendiffractiemetingen. De gemeten autonieuwvormingssnelheid voor twee verschillende thermische cycli bevestigden de gesimuleerde resultaten. Experimentele restaunienfracties na afkoelen waren binnen 1% van de gesimuleerde waarden wat kleiner is dan de experimentele onzekerheid.

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De verkregen resultaten uit implementatie van de ontwikkelde materiaalmodellen zijn in vele aspecten veelbelovend. De vier voorbeelden van experimentele validatie laten zien dat de fysische basis voor de in dit proefschrift gepresenteerde materiaalmodellen een algemene toepasbaarheid heeft. De aandacht voor de mechanismen voor grensvlakmobilitiet en nucleatie heeft een centrale rol gespeeld in dit succes. De weg naar een volledige thermisch-mechanische simulatie van gelast materiaal op microstructureel niveau heeft nog vele onbehandelde mijlen. De koppeling van microstructuur detail aan mechanische eigenschappen vraagt experimenteel of theoretisch gebaseerde fasenafhankelijke mechanische data. Vele andere aspecten, zoals de invloed van lokale spanningstoestand op nucleatie en niet-isotope mechanische eigenschappen dienen ook te worden bestudeerd. Optimalisatie van legeringscombinaties en/of procescondities uitgevoerd met de hier gepresenteerde methoden en modellen biedt vele mogelijkheden. Daarom kan dit werk beschouwd worden als een bouwsteen voor verder materiaalwetenschappelijk onderzoek naar de reactie van materiaal op lasser.
Zusammenfassung


Anschließend wird die treibende thermodynamische Kraft, die für die Bewegung der Grenzflächen verantwortlich ist, untersucht und ihre Einbindung in die Phasenfeldmethode erläutert. Das Kapitel schließt mit Beispielen zu Diffusion und Grenzflächenbewegung, welches die bestimmenden Faktoren der Bewegung der Grenzflächen sind.


In den Kapiteln 6 bis 8 werden Anwendungen der in den Kapiteln 3 bis 5 entwickelten Theorien und Verfahren behandelt. Dabei beschäftigt sich das Kapitel 6 mit dem Korngrenzschatten und der Rekristallisation in AISI316. Als austenitischer Edelstahl ist AISI316 ein ideales Medium zur Validierung des Modells zur Grenzflächenmobilität. Dieses Modell wird auf den Zeitskalen des Schweißens ( Sekunden) und Wärmebehandlungen (Stunden) nachgewiesen. Die Aktivierungsgenergie für die Grenzflächenmobilität zeigt sich dabei als 197,5 kJ mol⁻¹, was nur um 2,5 kJ mol⁻¹ unter dem theoretischen Wert liegt. Die Temperaturprofile werde mit einem angepassten doppelelliptischen Wärmequellemodell nach Goldak berechnet. Der Dual-Netz Ansatz wird zur Simulation der Mikrostruktur in verschiedenen Abständen zur Schweißzone verwendet. Die Rekristallisation wird ebenfalls simuliert, da sie eine wichtige Rolle in der Entwicklung der Mikrostruktur spielt. Die Kürze des Schweißtemperaturzyklus hat sich positiv auf die Bestimmung der Nukleationsdichte der rekristallisierten Körner ausgewirkt, da kaum Zeit zum Zusammenwachsen der Körner blieb.

In Kapitel 7 wird die Phasenumwandlung während des Schweißens simuliert. Neuere synchrotron-basierte Röntgen diffraktometrischen Messungen aus der Literatur lieferten dazu wertvolle m-situ zeitaufgelöste Daten zu den Phasenanteilen während des Schweißvorgangs.


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List of publications

R.G. Thiessen, I.M. Richardson

R.G. Thiessen, I.M. Richardson
*Modelling of Laser-Welded Joints and Microstructure - A Review and Outlook*

R.G. Thiessen, I.M. Richardson
*A Physically-based Model for Microstructure Development in a Macroscopic Heat Affected Zone: Grain Growth and Recrystallization*

R.G. Thiessen, J. Sietsma, I.M. Richardson
*A Dual-Mesh Strategy for Microstructure Development in Macroscopic Heat Affected Zone: Studies on AISI316 and AISI1005*

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E.M. van der Aa, R.G. Thiessen, M. Amirthalingam, J. Sietsma, I.M. Richardson
*Influence of Conventional- and Actively-Cooled Welding Thermal Cycles on the Microstructure Evolution of Dual-Phase Steel*
Curriculum Vitae

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THE END