MODELLING OF MICROSTRUCTURE IN NOVEL HIGH STRENGTH STEEL WELDS

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PREFACE

This dissertation describes work carried out between October 1988 and September 1992 at the Department of Materials Science and Metallurgy, Cambridge University, under the supervision of Dr. H.K.D.H. Bhadeshia. Unless appropriately referenced the work is my own and not the result of any collaboration. No part of this dissertation has been previously submitted for any degree or diploma at this, or any other University. The work described in Chapters 3 and 4 has been accepted for publication in the October 1992 edition of Materials Science & Technology.

This dissertation contains less than 60,000 words.

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NOMENCLATURE

- α Ferrite (body centered cubic iron or steel).
- α_1 Parabolic thickening rate constant for allotriomorphic ferrite growth.
- β Autocatalysis constant occurring in Bhadeshia's bainite transformation kinetics model.
- δ High-temperature ferrite (body centered cubic iron or steel)
- ϵ_1, ϵ_2 Material dependent constant used in modelling the cooling behaviour of welds.
 - γ Austenite (face centered cubic iron).
 - η $\,$ Arc transfer efficiency.
 - θ The maximum extent of bainite transformation that can form at a given temperature.
- λ_1, λ_2 Empirical constants arising in the modified bainite transformation kinetics model.
 - $\mu_C^{\alpha 0}$ Chemical potential of carbon in ferrite, referred to its standard state.
 - $\mu_{Fe}^{\alpha 0}$ Chemical potential of iron in ferrite, referred to its standard state.
 - $\mu_C^{\gamma 0}$ Chemical potential of carbon in austenite, referred to its standard state.
 - $\mu_{Fe}^{\gamma 0}$ Chemical potential of iron in ferrite, referred to its standard state.
 - ν Attempt frequency for nucleation.
 - ξ Normalised volume fraction of bainite *i.e.* v/θ .
 - ρ Molar area density of atoms in the planes of a martensitic embryo.
 - σ Total surface energy of a martensitic embryo.
 - σ_{y} Overall yield strength of a weld microstructure.
 - $\sigma_{\alpha_{\alpha}}$ The contribution of acicular ferrite to the yield strength of a weld microstructure.
 - $\sigma_{\alpha'}$ The contribution of martensite to the yield strength of a weld microstructure.
 - $\sigma_{\rm mic}$ The microstructural contribution to the strength of acicular ferrite.
 - au_{μ} Athermal component of the flow stress for interface dislocation motion during martensitic nucleation.
 - τ_i Incubation time for reaction initiation at a given temperature.
 - a Side length of hexagonal columnar austenite grains in a weld.
 - a^{α}_{C} Activity of carbon in the ferrite phase.
 - a_C^{γ} Activity of carbon in the austenite phase.
 - a_{Fe}^{α} Activity of iron in the ferrite phase.
 - a_{Fe}^{γ} Activity of iron in the ferrite phase.
 - Ae_1 The ferrite/(ferrite & austenite) equilibrium phase boundary.
 - Ae_3 The austenite/(ferrite & austenite) equilibrium phase boundary.
 - A Area of planes in a martensitic embryo.
 - b Magnitude of the Burgers vector in body centered cubic steel.

- $c_1^{\gamma\alpha}$ Concentration of carbon in austenite at a ferrite/austenite phase boundary in a ternary alloy.
- $c_1^{\alpha\gamma}$ Concentration of carbon in ferrite at a ferrite/austenite phase boundary in a ternary alloy.
- $c_2^{\gamma\alpha}$ Concentration of the substitutional solute in austenite at a ferrite/austenite phase boundary in a ternary alloy.
- $c_2^{\gamma \alpha}$ Concentration of the substitutional solute in ferrite at a ferrite/austenite phase boundary in a ternary alloy.
- C_2, C_3, C_4 Empirical constants arising in Bhadeshia's bainite transformation kinetics model.
 - D_{11} Diffusion coefficient of carbon in austenite.
 - D_{22} Diffusion coefficient of the substitutional solute in austenite in a ternary alloy.
 - \underline{D}_{11} Weighted average diffusion coefficient of carbon in austenite.
 - $E^{\rm str}$ Molar strain energy of martensite nucleation.
 - G^* Activation energy for nucleation of Widmanstätten ferrite or bainite.
 - G^{α} $\,$ Free energy of the ferrite phase.
 - G^{γ} Free energy of the ferrite phase.
 - $G^{\gamma \to \alpha'}$ Free energy change for transformation of austenite to ferrite of identical composition.
 - G_N The critical value of ΔG_m required for nucleation of displacive transformation products.
 - $\Delta G_m~$ Maximum free energy change per mole of precipitate phase.
 - ΔG_m^0 Maximum free energy change per mole of ferrite at the onset of the bainite transformation.

 ΔG_m^v Maximum volume free energy change on nucleation.

- ΔG^{chem} Molar chemical free energy change for the austenite to ferrite transformation during martensite nucleation.
 - G_{SW} The minimum driving force at which growth of Widmanstätten ferrite is possible.
 - $\Delta \overline{H}_{\alpha}$ Partial molar enthalpy for solid solution of carbon in ferrite.
 - $\Delta \overline{H}_{\gamma}$ Partial molar enthalpy for solid solution of carbon in austenite.
 - I_{WS} Nucleation rate of bainite at the W_S temperature (Bhadeshia 1982).
 - I_0 Nucleation rate of bainite at the W_S temperature, independent of the effects of autocatalysis (Bhadeshia 1982).
 - k Solute partitioning coefficient.
- K'_1, K_2 Empirical constants arising in the modified bainite transformation kinetics model.
 - \overline{L} Mean linear intercept of a series of random lines with the austenite grain boundaries in a sample.
 - n Number of planes in a given martensitic embryo.
 - N Nucleation rate of ferrite at the highest temperature of the lower. C–curve in a TTT diagram
 - q Thickness of allotriomorphic ferrite layers decorating prior austenite grains.

- Q Activation energy for martensitic nucleation, alternatively the electrical heat input to an arc weld.
- Q_d Molar enthalpy of diffusion.
- R Universal gas constant.
- $\Delta \overline{S}_{\alpha}$ Partial molar non-configurational entropy for solid solution of carbon in ferrite.
- $\Delta \overline{S}_{\gamma}$ Partial molar non-configurational entropy enthalpy for solid solution of carbon in austenite.
 - S_d Molar entropy of diffusion.
 - S_v Grain boundary surface area per unit volume.
 - T Temperature.
 - T_0 Initial temperature during the cooling of an arc weld, alternatively, the temperature at which austenite and ferrite of the same composition have identical free energies.
- $T_{\rm int}$ Interpass temperature for multi-run welds.
 - t_c Limiting time for growth of Widmanstätten ferrite before impingement with intragranularly nucleated transformation products occurs.
- T_H Highest temperature in the lower C-curve of TTT diagrams.
- T_h The temperature at which all otriomorphic ferrite formation begins during the cooling of a weld.
- t_i The length of the *i*th isothermal hold time when approximating a continuous cooling curve as a series of isothermal steps.
- t_m Experimentally measured time taken to form a given volume fraction of bainite.
- $t_{\rm p}$ $\,$ Predicted time taken to form a given volume fraction of bainite.
- u Volume of a bainitic sub-unit.
- v Volume fraction of ferrite in a ferrite/austenite mixture.
- v^* Activation volume of a martensitic nucleus.
- V_{α_a} Volume fraction of acicular ferrite in a microstructure.
- V_{α} Volume fraction of all otriomorphic ferrite in a microstructure.
- V_{α_W} Volume fraction of Widmanstätten ferrite in a microstructure.
- $V_{\alpha'}$ Volume fraction of martensite in a microstructure.
- $V_{\rm int}$ Velocity of the α/γ interface during allotriomorphic ferrite growth.
- w_{α} Carbon-carbon interaction energy in ferrite.
- w_{γ} Carbon-carbon interaction energy in austenite.
- W Total energy of a martensitic embryo.
- \overline{x} Carbon mole fraction of the bulk alloy.
- X General representation of the substitutional solute in a ternary alloy steel.
- x^{α} Carbon mole fraction of ferrite.

- x^{γ} Carbon mole fraction of austenite.
- $x^{\alpha\gamma}$ Carbon mole fraction of ferrite at the austenite/ferrite interface.
- $x^{\gamma\alpha}$ Carbon mole fraction of austenite at the austenite/ferrite interface.
- x_l Liquidus composition (mole fraction).
- \boldsymbol{x}_m . The most probable ferrite nucleus carbon mole fraction.
- x_{N_0} Maximum austenite composition for which nucleation of ferrite by a displacive mechanism is possible.
 - x_s Solidus composition (mole fraction).
- $x_{T'_0}$ Composition at which austenite and ferrite (with a stored energy of 400 J mol⁻¹) have identical free energy.
 - Z Position of the α/γ interface during allotriomorphic ferrite growth.

CHAPTER 1

Introduction

The aim of this chapter is to provide a brief background to the physical metallurgy of steel and to the process of welding. Both of these subjects form the cornerstone of the research topic. The theoretical concepts relevant to phase transformations work presented in later chapters are also included here.

1.1 An Introduction to the Welding Process

1.1.1 Welding Processes

The principle of fusion welding is as follows. Two pieces of metal are joined by introducing molten filler metal into the gap between them at a sufficiently high temperature to achieve some melting of the pieces being joined. Subsequent solidification of the weld metal ensures a continuous joint in which the grains of the weld metal tend to grow directly from those of the base plate.

The introduction of the filler metal can be achieved in one of many ways. One of the most common of these is arc welding, in which the heat source is an electric arc. The filler metal is introduced by the transfer of molten metal from the tip of the electrode into the joining area, where it forms a pool beneath the arc. In this process the electrode is gradually consumed, the bulk of the metal in the weld pool coming from the electrode, with some also coming from the base plate from regions beneath the arc, where its melting temperature has been exceeded. The transfer of the metal from the electrode to the weld pool occurs by a combination of many processes. These involve the gravitational pull on molten metal at the electrode tip, the electromagnetic Lorentz force resulting from the force between two current carriers, and detachment of molten metal from the electrode when contact is made between the tip and the weld pool (Lancaster, 1970). The welding current usually lies in the range 100-1000 A and the voltage in the range 10-50 V.

There are many different variants of the arc welding processes. Depending on the process the molten metal in the weld pool is protected from the surrounding environment either by shielding gasses (gas metal arc, GMA welding), or alternatively, the protection may be via a flux which forms a slag on top of the weld pool. The gasses in the air, as well as moisture, have a potentially damaging effect on the properties of the weld and so it is essential to control the extent of gas pick-up from the atmosphere. The slag therefore serves as a protective covering and can indeed provide a chemically reducing environment. Gases given off by the slag can also aid metal transfer from the electrode the weld pool.



Figure 1.1 Schematic representation of welding processes, (after Easterling 1983).

The flux derives from the electrode coating in manual metal arc welding (MMA), from an electrode core, in the case of flux cored wire welding (FCAW), or is fed directly onto the welding surface covering the arc and the electrode as in submerged arc welding (SAW), in which case the electrode can be bare. These processes are shown schematically in Figure 1.1.

This work is primarily concerned with weld deposits produced by the submerged arc technique in which flux is gravity-fed from a hopper into the path of the moving electrode. The process is very suitable for highly automated, high speed welding with large deposition rates being possible (Deb, Challenger & Therrein, 1987).

For the submerged arc process the slags typically contain silica, alumina, rutile, magnesia, flurospar, lime, manganese oxide and various deoxidants. Some oxygen is bound to ingress into the molten metal during the welding process (Grong & Matlock, 1986). The role of deoxidants is to form oxides that will separate into the slag. As the metal cools some of these deoxidation products will become trapped in the solidifying metal as inclusions. These can have an important effect on the subsequent development of the weld microstructure, as will be discussed later.

The chemical composition of the filler metal has a profound effect on the resultant microstructure of the weld metal, and therefore on the mechanical properties as well. The electrode composition determines the composition of the metal deposited into the weld pool, and together with dilution from the base plate, this controls the weldment substitutional alloy content. The carbon content of the weldment is also determined by the electrode. In general however, the electrode has a higher carbon content than the eventual deposit since oxidation of carbon occurs during the welding.

Nitrogen enters the weld pool mainly from the air. The different solubility of nitrogen in δ ferrite and austenite can cause the precipitation of nitrides as the weld metal transforms from δ to γ during cooling. Hydrogen can be inadvertently introduced through the breakdown of moisture under the influence of the electric arc, an effect that is strongly dependent on the moisture content of the flux. The extremely high diffusivity of hydrogen means that a lot of it escapes from the weld surface, however significant quantities can diffuse into the adjacent plate, causing heat affected zone cracking. Because of hydrogen's highly damaging effect on weld metal properties it is essential to eliminate its presence as much as possible. For particularly thick sections hydrogen poses even more of a problem since the surface loss of the gas is less effective in such cases.

1.1.2 The Welding Thermal Cycle

The influence of the arc extends beyond the boundary of the weld pool into the so-called heat-affected zone of the base plate. Different chemical and physical changes are expected in the weld deposit and base plate depending on the thermal experience and other characteristics of each region. As the weld is moved along the abutting plate a steady state is established between the melting and solidification processes. The shape and size of the weld pool will depend, for example, on the thermal diffusivities of the plate and molten metal, as well as the speed of welding and the heat input from the arc.

Efforts at modelling the thermal profiles resulting from welding processes have been successful in accounting for much of the behaviour exhibited by real welds. The well known work of Rosenthal (1958) considers welding as the action of a moving point heat source on a flat isotropic and homogeneous plate. In so doing the effects of changes in thermal behaviour with temperature and changes of state are ignored, as is the latent heat absorbed and released on melting and cooling. In spite of this the results are very revealing in describing the effects of the weld pass.

One interesting result is that in most cases the speed of welding exceeds that of thermal diffusivity, causing a build up of the isotherms ahead of the heat source, resulting in very steep thermal gradients in the region of the pool causing base plate melting. The heat profile of a typical submerged arc weld on a steel plate is shown in Figure 1.2.



Figure 1.2 Heat profile for a submerged arc weld on a steel plate (after Easterling, 1983).



Figure 1.3 The iron-carbon phase diagram, (after Anderson et al., 1985)

1.2 An Introduction to the Metallurgy of Steel

1.2.1 Pure Iron and its Allotropes

At atmospheric pressure pure iron has two allotropic forms. At low temperatures (*i.e.* < 912°C) the atoms form a body centered cubic structure known as ferrite (α), which is also the stable form at higher temperatures (*i.e.* > 1394°C). At intermediate temperatures the face centered cubic structure is the most stable, and this is called austenite, designated γ . Iron can also exist as a hexagonal close packed structure, but this is only possible at very high pressures (130 kbar). This form is known as ϵ and is the densest form of iron. Melting occurs at 1538 °C.

Iron also shows another transition. At 770 °C there is the Curie transition, which involves a change from the high temperature paramagnetic ferrite to the lower temperature ferromagnetic ferrite.

1.2.2 The Effect of Carbon and the Iron-Carbon Phase Diagram

Carbon is an interstital alloying element. Rather than replacing iron in the lattice it sits in the spaces between the iron atoms and is much more soluble in austenite than in ferrite. Varying the carbon content of steel has a significant effect on the phase transition temperatures as can be seen from the phase diagram shown in Figure 1.3. At higher temperatures δ ferrite shows much greater carbon solubility than the very low value that α ferrite displays. At 1495 °C the δ /liquid phase field gives way to a γ /liquid field. Steels cooling through this region are said to undergo a peritectic reaction. At the transition temperature (1495 °C) three phases δ , γ and liquid can coexist as the δ and liquid react to generate austenite.

Increasing quantities of carbon confer stability to the austenite so that this field dominates the intermediate temperature range of the low carbon Fe–C diagram. A two phase α/γ region is formed as well as a similar field for the equilibrium between austenite and cementite, which is an iron carbide.

At low temperatures it can be seen that the equilibrium condition for steels with carbon contents greater than 0.0218 (wt%) is as a two phase mixture of ferrite and cementite. At just below 727 °C a steel of composition Fe–0.77 C (wt%) will be simultaneously supersaturated with respect to the ferrite and cementite phases. This results in the equilibrium structure known as pearlite where fine lamellae of α and Fe_3C form co-operatively from austenite. The lamellae are in fact interconnected in three dimensions so that each pearlite colony is actually a bicrystal of ferrite and cementite.

1.2.3 Substitutional Alloying Elements and their Effect

Another kind of alloying element is one which, in small quantities, can enter into the iron lattice replacing the host atom in the process. These elements are known as substitutional solutes. Those most commonly used in steel are silicon, manganese, nickel, molybdenum, chromium and vanadium. The presence of these elements affects the free energy change associated with the various phase transformations, therefore alloying can be used to change the transformation behaviour of steel. Substitutional alloying elements affect the Fe–C phase diagram by expanding or contracting the stability fields of the various phases, as well as changing the transition temperature between these phases. A conceptually convenient, though not rigorous notion is that those elements which expand the austenite phase field (e.g. C, Mn, Ni) are called austenite stabilisers, and those promoting ferrite stability are called ferrite stabilisers (e.g. Mo, Cr). Substitutional alloying elements can also cause the introduction of new phases such as alloy carbides.

As well as their thermodynamic effect, alloying elements usually have different solubilities in the various phases. This can necessitate redistribution during transformation. Diffusion is therefore necessary for equilibrium to be maintained. Under the correct conditions alloyed steels can be encouraged to transform at rates that do not allow for this complicated redistribution of alloying elements to take place, thereby adding further to the range of transformation structures that can be produced.

1.3 Phase Transformations in Steel

1.3.1 Equilibrium Transformations

The phases shown in the iron-carbon are the equilibrium phases, although graphite is in fact more stable that cementite. Equilibrium represents the absolute minimum free energy configuration at a given temperature and is in fact an ill-defined concept in the sense that one may have to wait for unacceptably long times for equilibrium to be achieved. A local minimum in free energy, however, gives a metastable equilibrium which follows the same thermodynamic theory. So for example, within the time scale of welding we need not worry about graphitisation and the metastable cementite phase is more appropriate for consideration.

As far as is known the phase diagram gives the minimum free energy phase or phase mixture for any given temperature. Transformation from one phase to the other must occur ideally with very slow cooling for the equilibrium structure to be attained. In practice, with sufficiently slow cooling the phases equilibrium can be maintained locally at the transformation interface, even if concentration profiles exist ahead of the advancing interface. The nucleation process in all real solid state transformations in steel is heterogeneous, occurring at defects such as grain boundaries, dislocations or foreign bodies such as non-metallic inclusions. In such cases an energetic advantage is obtained by eliminating a portion of the matrix/interface during nucleus formation.

1.3.2 Metastable Reconstructive Transformation in Steel

Metastable phases can be formed at the expense of the thermodynamically favoured phase if there is a suitable kinetic obstacle to the latter's formation. For example, a large activation energy for nucleation, or a slow growth process can inhibit the formation of the stable phase. In situations such as these, provided that there is sufficient thermodynamic driving force, metastable phases which can nucleate and grow at greater rates can form.

Considering the case of a plain carbon steel, the chemical potential of carbon and iron in ferrite of a given composition (\bar{x}) is given by the values of the intercept of a tangent line to the ferrite free energy curve at \bar{x} with the free energy axis at x = 0 and x = 1 respectively. At a given temperature the compositions of a two phase equilibrium mixture will be that which gives equal chemical potential to all components across the phase interface. This condition is represented by the case where two free energy curves have the same tangent line. For the decomposition of a supersaturated austenite into a two phase α/γ mixture as shown in Figure 1.4, the free energy change ΔG will be equal to the separation of the parent free energy curve at \bar{x} and the line joining the product curves at their respective compositions x_{α} and x_{γ} . As Figure 1.4 shows, for a metastable transformation in which the modified ferrite curve is displaced along



Figure 1.4 The free energy change on formation of a metastable phase showing the differences between the equilibrium and metastable equilibrium compositions

the free energy axis the magnitude of the free energy change $\Delta G'$ is reduced, and the tangent line touches the curves in new positions, indicating that the metastable equilibrium phase compositions differ from the equilibrium values. A characteristic of metastable transformations is that the composition of the matrix in metastable equilibrium with the precipitated phase lies closer to the bulk composition than does the equilibrium matrix composition. The importance of this fact will be explained later when considering the bainite transformation in steels.

Austenite

An example of metastable austenite formation is in steels where δ is the stable phase at high temperatures. Austenite can sometimes form directly from the liquid. This is especially true in welds if cooling rates are high and the solute partitioning coefficient is closer to unity for austenite than ferrite. The solute partitioning coefficient k is given by

$$k = x_s / x_l$$

where \boldsymbol{x}_s and \boldsymbol{x}_l refer to the solute mole fraction of the solidus and liquidus respectively.



Figure 1.5 Extrapolation of the phase boundaries into regions of metastability

Ferrite

Another type of metastable transformation involves the formation of a phase outside the temperature or composition range for which it is the equilibrium phase. It may be that the growth rate of the metastable phase exceeds that of the equilibrium phase. As demonstrated by Figure 1.5 the phase boundaries can be extrapolated in such cases to give the metastable equilibrium phase compositions outside their normal range of stability.

A special kind of metastable transformation from austenite to ferrite can occur in alloy steels containing both substitutional and interstitial solutes. Let the interstitial solute be carbon, and let X represent the substitutional solute element. At the interface between the austenite and ferrite partitioning of the substitutional solute and carbon occurs. The velocity $V_{\rm int}$ of the interface must of such a value as to satisfy the flux equations for both solutes simultaneously *i.e.*

$$\left(c_1^{\gamma\alpha} - c_1^{\alpha\gamma}\right)V_{\rm int} = D_{11}\nabla c_1$$

and

$$(c_2^{\gamma\alpha} - c_2^{\alpha\gamma}) V_{\rm int} = D_{22} \nabla c_2$$

where c_1 and c_2 are the concentrations of carbon and X respectively, with D_{22} being the diffusion coefficient of the substitutional solute. The superscripts $\alpha\gamma$ and $\gamma\alpha$ denote the *interface* values of c_1 and c_2 in the ferrite and the austenite respectively. Because $D_{11} >> D_{22}$ the equilibrium values of the interface compositions will not satisfy the transport equations. Modified values are adopted, which can fall into one of two regimes, depending on the degree of austenite supersaturation.

Isothermal sections of a ternary phase diagram Fe–X–C are shown in Figure 1.6, where X is a substitutional alloying element. It is demonstrated in the diagram how the interface compositions are chosen so that the ferrite and austenite compositions are equilibrium-related, though they are not the equilibrium compositions for the alloy composition as a whole. In Figure 1.6 diagram (a) illustrates the case for small supersaturations. The austenite composition of the interface lies along the carbon isoactivity line, resulting in a very small activity gradient driving the diffusion of carbon, producing a small carbon flux. The activity gradient of X is steeper, and under these conditions appreciable partitioning of X is possible. In diagram (b) the case for high supersaturations is shown. The interface compositions are chosen this time to give the concentration of X in the ferrite very close to the value for the bulk alloy. This results in negligible partitioning of the substitutional solute, and hence its diffusion field can be very short, giving a sharp concentration spike at the interface. Under these conditions the interface can advance rapidly, and appreciable partitioning of carbon is possible.

In this way, two regimes are found, one in which there is considerable diffusion of carbon ahead of the interface but negligible partitioning of X, and one where there is only a shallow composition gradient of carbon ahead of the interface and the substitutional alloy element partitions over a larger range. These regimes are named 'Negligible Partitioning Local Equilibrium' or NPLE and 'Partitioning Local Equilibrium' or PLE respectively. In both cases there continuity of chemical potential across the interface.

At even faster growth rates it becomes impossible for the maintenance of equilibrium of the substitutional alloying elements. The transformation then proceeds without the partitioning of X at all, even at the interface. Free energy minimisation is then achieved with respect to carbon only, with the constraint that the Fe/X ratio is constant everywhere. This condition is known as paraequilibrium and is especially useful when considering the transformation of austenite to ferrite in steel welds.

1.3.3 Metastable Displacive Transformations in Steels

Thermodynamic equilibrium is usually attained by the diffusion of atoms into the lowest energy sites. For this process to occur requires sufficient atomic mobility for atoms to overcome the potential energy barrier surrounding their existing higher energy site. At lower temperatures this becomes increasingly difficult as the diffusivity decreases. The attainment of equilibrium then requires extremely slow cooling, usually at impractical rates. A mechanism which allows





Figure 1.6 Ternary Fe–C–X phase diagrams demonstrating the regimes in which PLE and NPLE transformation can occur, and the choice of interface compositions

phase transformation without the need for diffusive jumps can under those circumstances have a kinetic advantage.

Figure 1.7 shows the mechanism by which the transformation from austenite to ferrite can be achieved without the need for atoms to move a distance as large as an inter-atomic spacing. Considering two unit cells of face centered cubic austenite γ as shown in Figure 1.7 a body centered tetragonal cell (bct) can be defined within the same structure. Representing the base vectors of the austenite cell as \mathbf{a}_{γ} , \mathbf{b}_{γ} and \mathbf{c}_{γ} and those of the new ferrite cell as \mathbf{a}_{bct} , \mathbf{b}_{bct} and \mathbf{c}_{bct} the two cells can be related as follows

$$\mathbf{a}_{\mathrm{bct}} = \frac{1}{2} \left(\mathbf{a}_{\gamma} - \mathbf{b}_{\gamma} \right)$$
$$\mathbf{b}_{\mathrm{bct}} = \frac{1}{2} \left(\mathbf{a}_{\gamma} + \mathbf{b}_{\gamma} \right)$$

$$\mathbf{c}_{\mathrm{bct}} = \mathbf{c}_{\gamma}$$

Transformation is then accompanied by expansion along the \mathbf{a}_{bct} and \mathbf{b}_{bct} and contraction along \mathbf{c}_{bct} producing a cubic or a tetragonal ferrite lattice. This is known as the Bain Strain.

Diffusion is not necessary to achieve the change from fcc to bcc although it should be noted that additional deformation is required in order to ensure that the strain energy is minimised. Thus the *macroscopic* shape change is not in fact the one described by the Bain Strain, but is in fact an invariant plane strain (IPS).

Because of the large shear component of the IPS the ferrite, when it forms under constraint, has a large strain energy. If, at a given undercooling below Ae_3 there is enough driving force to overcome this strain energy then this mechanism becomes feasible.

Three forms of ferrite (with a fourth being an additional variant of one form) can grow by a displacive mechanism.

Widmanstätten Ferrite

The typical morphology of Widmanstätten ferrite is shown in Figure 1.8. Formation of this phase occurs at rather small undercoolings below Ae_3 (Bhadeshia, 1985). Upon transformation of polished specimens surface relief is observed, often doubly tilted, tent-like, but sometimes singly tilted, consistent with an invariant plane strain (Watson & McDougall, 1973). These observations led to the view that Widmanstätten ferrite grows by a displacive transformation. It was shown though that there was insufficient free energy for the formation of a single plate by such a mechanism at such low undercoolings below the Ae_3 temperature (Aaronson *et al.*, 1975). Transformation in fact involves the mutually accommodating growth of two plates back-to-back, minimising the strain energy of formation. The adjacent plates, illustrated in



Figure 1.7 The Bain Strain lattice transformation



Figure 1.8 Typical Widmanstätten ferrite morphology

Figure 1.8, are found to be two closely related variants (Bhadeshia, 1980), each having a slightly different orientation relationship with the surrounding austenite. The effect of the mutual accommodation is to reduce elastic the distortion around the plates as is shown in Figure 1.8, thereby reducing the strain energy to about 50 J mol⁻¹ (Bhadeshia, 1981a).

Widmanstätten ferrite grows under paraequilibrium conditions, the carbon partitioning occurring *during* transformation, whereas the substitutional lattice is merely displaced, with no substitutional solute partitioning. On an optical scale, a Widmanstätten ferrite plate has the appearance of a thin wedge which grows as the tip advances, the wedge shape being due to the slightly different interfacial orientation that the adjacent plates in the Widmanstätten ferrite wedge have with the austenite.

Bainite

Perhaps the most interesting of all the metastable transformations in steels is bainite. The mechanism of transformation has been difficult to elucidate and has been hotly debated. One school of thought maintains that bainite is the product of a reconstructive transformation, with the opposing side holding the view that transformation is displacive and diffusionless but that the decarburisation of ferrite occurs after transformation (Aaronson, 1962; Ko & Cottrell, 1952; Heheman, Kinsman & Aaronson, 1972; Kinsman, Eichen & Aaronson, 1975; Bhadeshia & Edmonds, 1979, 1980). A self-consistent picture has now emerged in which bainite is established as a shear transformation where formation involves the repeated nucleation and growth of platelets which form aggregates known collectively as sheaves, shown schematically in Figure 1.9. The appearance of a sheaf under optical microscopy is that of a thin wedge. With transmission electron microscopy the individual plates or sub-units within a sheaf become observable. Sheaves appear to grow by a lengthening and thickening process, which if fact results from the nucleation of further sub-units both at the tips of previously formed plates, and side by side with them. Nucleation at the plate tips is thought to be the more effective of the two processes, so it is not surprising to observe sheaves with an overall plate-like appearance (Bhadeshia & Christian, 1990).

Individual sub-units form with an initial full supersaturation of carbon (Bhadeshia & Edmonds, 1979, 1980). The ferrite then decarburises either by the diffusion of carbon into the surrounding untransformed austenite, and/or by precipitation of carbides within the ferrite. It is by these two decarburisation mechanisms that the two forms of classical bainite are distinguished. Carbon partitioning to the austenite leads to the formation of upper bainite, with its carbide-free ferrite plates. Precipitation of carbides within the ferrite leads to lower bainite. The time taken to decarburise by diffusion when compared to that required to precipitate carbides in ferrite is what distinguishes the two mechanisms (Takahashi & Bhadeshia, 1990).



Figure 1.9 Schematic representation of a bainite sheaf.

At higher temperatures where decarburisation by diffusion is fast, upper bainite forms. The carbon enriched austenite then either decomposes to a ferrite/carbide aggregate, transforms to martensite or is retained as austenite, depending on the alloy composition and the transformation conditions. As the temperature decreases, the time to decarburise by diffusion increases until a threshold point is reached when carbide nucleation and growth can occur inside the ferrite within a shorter time interval. This is the mechanism that leads to lower bainite. Both mechanisms are illustrated in Figure 1.10.

Thermodynamic analysis of the conditions of formation has provided supportive evidence for the diffusionless reaction mechanism. Transformation is not observed when it becomes energetically impossible to form supersaturated bainitic ferrite with its associated strain energy of 400 J mol⁻¹. This thermodynamic condition can occur either because the undercooling below Ae_3 is insufficient, or because, as a result of prior ferrite formation, the carbon enrichment of the untransformed austenite has reached a level that reduces the free energy change of the γ/α transformation below the critical level. This latter condition leads to a phenomenon known as *incomplete reaction* where, at a given temperature, the volume fraction of bainite formed, as well as the austenite composition at reaction termination, is below the value predicted by equilibrium or paraequilibrium conditions. If the reaction were reconstructive in character then transformation would be expected to proceed until the austenite carbon content reached the



Figure 1.10 The development of carbides in upper and lower bainite

paraequilibrium Ae_3 boundary.

It can also be demonstrated that, even on the finest scale, there is no partitioning of substitutional alloying elements at the bainitic ferrite/austenite interface (Bhadeshia & Waugh, 1981).

Bainitic steels find great use in engineering because of their combination of toughness and strength. Bainitic weld metals are used extensively in the power generation industry because of its stable microstructure, conferring high temperature stability to the joint.

Acicular Ferrite

Acicular ferrite first came to prominence as a phase forming in weld deposits. Appearing to nucleate at non-metallic inclusions present in the weld pool (Ito & Nakanishi, 1976), the phase formed at intermediate temperatures, between that of allotriomorphic ferrite and martensite formation. The typical morphology of acicular ferrite is shown in Figure 1.11. Originally, it was speculated that acicular ferrite was a form of Widmanstätten ferrite (Ricks, Howell & Barrite, 1982), but it has recently become apparent that it is actually an intragranularly-nucleated form of bainite.

With its fine microstructure of disorganised plates it imparts good toughness and strength to weld metals and is therefore a highly desirable phase. By presenting a tortuous path to an



Figure 1.11 Morphology of Acicular Ferrite

advancing crack more energy is absorbed per unit of propogation, improving toughness (Ito & Nakanishi, 1982).

Weld deposits are notable for the very large, columnar prior austenite grains. These are a result of the high temperatures and large thermal gradients within the weld pool which undergoes cellular solidification to large δ grains, which then transform to the columnar γ grains. A large austenite grain size is one requirement for the stimulation of intragranular nucleation on inclusions since the number density of competing grain boundary nucleation sites is then relatively decreased. This has been confirmed by studying the transformation behaviour of reheated weld metals. It is found that after austenitising at low temperatures, the small γ -grained specimens transform to bainite. Under the same conditions, high temperature austenitisation, and the accompanying large austenite grains, gives a predominantly acicular ferrite microstructure (Yang & Bhadeshia, 1987). Acicular ferrite also shows a transformation surface relief consistent with an IPS shape change (Strangwood & Bhadeshia, 1987) and an incomplete reaction, similar to bainite (Yang & Bhadeshia, 1987). As well as these similarities, it has been demonstrated that in the same way that upper or lower bainite are found in wrought steels, upper and lower acicular ferrite can be generated by altering the weld chemistry (Sugden & Bhadeshia, 1989). However, lower acicular ferrite is not normally observed in real welds, since weld metal carbon concentrations are usually kept low in order to avoid the formation of brittle, high-carbon martensite.

It appears then, that acicular ferrite is identical to bainite, but nucleated on inclusions. The acicular ferrite plates do not normally cluster as sheaves, presumably because the hard impingement of plates with those nucleated on neighbouring sites makes the development of a sheaf impossible. It is common to see plates nucleating autocatalytically *i.e.* plate nucleation on previously transformed regions. In this manner the number of sites for nucleation increases as transformation proceeds – this is the essence of autocatalysis. It is not yet known whether nucleation is aided by the stress field around the plate, by the dislocations that form in the austenite as a result of the plastic accommodation of the plate's shape change, or whether existing plates simply provide a surface for heterogeneous nucleation.

Thermodynamics of Widmanstäten Ferrite and Bainite Nucleation

Bainite and Widmanstätten ferrite are displacive transformations which form at relatively small undercoolings, above the temperature at which nucleation can occur by a displacive diffusionless process (*i.e.* the M_S temperature, at which martensite occurs). The nucleating mechanism for these reactions must therefore be slightly different to that of martensite and this difference is the essence of the problem of rationalising the transformations in steels.

Isothermal transformation diagrams in steels show the regimes in which reconstructive and displacive reactions occur. In lightly alloyed steels the temperature ranges over which the different reaction mechanisms operate often overlap giving the overall appearance of a single C– curve. Increasing the substitutional solute content of the steel clarifies the picture by separating the reconstructive and displacive transformation ranges so that each mechanism has a separate C–curve. As the alloy content is increased the lower C–curve develops a flat top indicating that the nucleation of ferrite decreases very rapidly over a very narrow range of temperature increase.

The work of Steven and Haynes (1956) provides a rich dataset for the highest temperature T_H in the lower C-curve of TTT diagrams. Depending on the alloy content of these steels T_H can correspond to the formation of either bainite or Widmanstätten ferrite. The data were used to investigate the relationship between the free energy change and the temperature at which formation became possible (Bhadeshia, 1981a).

Nucleation theory states that for the formation of a very small amount of precipitate the composition change in the matrix is negligible, therefore the most likely precipitate composition is that which allows the maximum free energy change under these conditions (Hillert, 1953). This change is termed ΔG_m and is discussed in detail in section 2.1.2.

Bhadeshia plotted the values of $\Delta G_m \{T_H\}$ against T_H . As is shown in Figure 1.12 the results regress onto a single straight line. The implications of this result are that



Figure 1.12 Comparison plots of the relationship between ΔG_m and the free energy change for no composition change $\Delta G^{\gamma \to \alpha'}$ against the highest temperature for displacive nucleation.

- a) Since a single line is found to represent all the data, Widmanstätten ferrite and bainite must develop from the same nucleus, but the phase into which the nucleus eventually develops must depend on the conditions during growth.
- b) The linear relationship indicates (as shown later) that the activation energy nucleation is linearly dependent on the ΔG_m .
- c) Carbon partitioning occurs during the nucleation process. This is the essential difference between the nucleation of Widmanstätten ferrite and bainite and that of martensite (discussed in detail in section 2.1.5).

These findings can be rationalised if it considered that at T_H (the temperature at which displacive nucleation is first possible) there is a constant nucleation rate N

$$N \propto \nu \exp\left\{-\frac{G^*}{RT}\right\}$$

where ν is the attempt frequency, G^* is the activation energy.

In order to obtain an expression for the relationship between the activation energy for nucleation and the free energy change at T_H consider that

$$G^*\{T_H\} \propto \beta T_H$$

it is desired to find

$$G^*\{T_H\} = f\{G_m\{T_H\}\}$$

hence

$$\beta T_H = f\{G_m\{T_H\}\}$$

When Bhadeshia plotted $G_m\{T_H\}$ versus T_H he obtained a linear relationship, which implies

$$T_H = mG_m\{T_H\} + c$$

where m and c are constants. This in turn implies

$$G^* = m'G_m\{T_H\} + c'$$

This result is consistent with the theoretical expression for the activation energy when 'nucleation' is by a displacive mechanism involving the growth of pre-existing embryos (Olson & Cohen, 1976).

Martensite

The only truly diffusionless transformation forming in steel, martensite occurs when there is sufficient thermodynamic driving force to both nucleate and grow displacively without any need for carbon diffusion.

Martensite forms as plates which can propagate right across austenite grains, though they are never observed to cross the grain boundaries. Between the plates it is common to see thin layers of retained austenite. The shape change produces characteristic surface relief consistent with a macroscopic invariant-plane strain deformation. Carbon within the austenite as it transforms remains in solution in the martensite, the diffusion velocity at the transformation temperature being small in comparison to the growth velocity.

By holding a martensitic structure at higher temperatures, carbide precipitation is encouraged. This process (tempering) relieves some of the strain due to the distorsions around the carbon atoms in the martensite. It is possible for some low alloy steels to autotemper *i.e.* the martensite is almost instantly tempered as the transformation proceeds.

The nucleation of martensite is believed to occur when a suitable coherent fault in the austenite matrix is induced to grow, by the propogation of the interface dislocations, under the

stress provided by the chemical free energy change. It is expected that a variety of suitable faults are present in austenite *e.g.* at grain boundaries. Each fault requires a different driving force in order to activate it and hence there is a distribution of fault potency. This fact is significant when considering steels that transform with burst characteristics *i.e.* with a very large autocatalytic effect. With such steels, at a given temperature only those faults with a low enough activation energy can form nuclei, and these then initiate a certain degree of transformation. It is necessary to lower the temperature, thereby increasing the driving force and stimulating less potent faults to induce further nucleation and hence increase the fraction of martensite. In this manner martensite shows athermal characteristics. It is possible however for isothermal martensite formation to occur in some steels (Olson & Cohen, 1976).

1.4 Development of Microstructure During the Cooling of Weld Metal.

1.4.1 Solidification

In general low alloy steel welds solidify as δ ferrite. Growth of this phase is epitaxial from the base plate grains at the fusion boundary for low alloy steels (Davies & Garland, 1975).

Transformation to δ ferrite occurs with a cellular δ /liquid front (Calvo *et al.* 1963). Since near the fusion boundary the base plate grains are coarsened by the high temperatures this gives rise to a δ ferrite grain cross section much larger than that of the original plate.

Under certain conditions of high cooling rate it is possible for the steels to solidify directly as metastable γ . This is especially true in cases where the solute partitioning coefficient for the austenite is closer to unity than that of ferrite (Fredriksson, 1976, 1983), in which case the growth rate of austenite may exceed that of the ferrite. It is also possible for highly alloyed steels to have austenite as the stable high temperature phase, and consequently solidify as γ .

The diffusivity of substitutional solute elements is generally higher in ferrite than in austenite, enabling segregation effects to be minimised (Fredriksson, 1976, 1983). Any segregated regions are found at the δ/δ boundaries. Non-metallic inclusions tend to gather at solidification cell boundaries. Subsequent transformation to austenite then brings these inclusions into the centre of the grains where they can play an important role in nucleating other phases (Sugden & Bhadeshia, 1988). The preferential presence of inclusions at austenite boundaries would, on the other hand, incorporate them within the allotriomorphic ferrite which forms at lower temperature. This phase is relatively brittle at best, without the detrimental presence of inclusions. In these ways then it is apparent that solidification as δ ferrite is desirable.

At any given point during welding, the moving heat source causes a variation of temperature with time. Grain solidification generally occurs along the direction of maximum heat flow *i.e.* down the steepest thermal gradient. However, as the temperature gradient also changes with time, the austenite grains which evolve from the δ tend to curve away from the δ boundaries where they first nucleated (Dadian, 1986). It is by this process that segregated regions and inclusions, previously at δ boundaries, are incorporated into the body of the austenite grains. This is shown schematically in Figure 1.13.

Since the nucleation and growth of austenite occurs at the δ -ferrite boundaries the austenite grain size is in general smaller that of the δ -ferrite. The situation might change if the austenite grains coarsen during cooling. To some extent the eventual γ grain size is influenced by the the plate grain size because of the epitaxial solidification. The degree of coarsening of the hot base plate grains at the fusion line is therefore important in this context. The eventual size of the γ grains does have a profound effect on subsequent transformations occurring in the cooling weld metal (Bhadeshia, Svensson & Gretoft, 1985).


Figure 1.13 Schematic representation of the relative growth orientations of δ and γ grains

Allotriomorphic ferrite begins to form when the weld metal cools below the Ae_3 temperature. In most cases, because of the high cooling rates in welds, growth occurs under paraequilibrium conditions (Bhadeshia *et al.* 1985), with no redistribution of substitutional solute atoms, though NPLE and PLE growth can occur. Nucleation occurs heterogeneously at the austenite grain boundaries, and because of the energetic benefits of doing so, growth along these boundaries is fast, decorating the austenite grains (Bhadeshia, 1991). When a uniform polycrystalline layer of ferrite has been formed, covering all the austenite boundary surface, growth can only proceed into the grain. It has been shown that the thickness of allotriomorphic ferrite formed is insensitive to austenite grain size suggesting that nucleation is not the dominant factor in determining the transformation kinetics of allotriomorphic ferrite (Dallum & Olson, 1989).

Nucleation at a γ/γ boundary means that the ferrite is in contact with two differently oriented austenite grains. The resulting difference in crystallographic orientation between the ferrite and the two austenite grains manifests itself in the interface and growth characteristics. As a rule, there will be a side with good matching of close packed directions and planes and there will be a poorly matched side with and incoherent interface. On the well matched side the interface will propagate by the movement of incoherent ledges on the well matched interface, parallel to it. On the poorly matched side growth is by movement of the incoherent interface normal to itself.

Under paraequilibrium conditions growth is carbon diffusion-controlled. For a fully decorated austenite grain the ferrite allotriomorph growth can then be treated as a one-dimensional diffusion-controlled thickening.

As the temperature decreases transformations by diffusional processes become sluggish, and once displacive transformations are thermodynamically feasible, they can dominate. The first displacive reaction to occur is Widmanstätten ferrite formation. This phase can nucleate directly on the γ/γ boundary or on the newly formed allotriomorphs. These two kinds of Widmanstätten ferrite are called primary and secondary Widmanstätten ferrite respectively. With the appearance of a thin wedge, though actually two mutually accommodating plates, growing rapidly in the direction parallel to its length, plates can grow right across austenite grains in a matter of seconds unless impingement with intragranularly nucleated products stifles growth.

The intragranular nucleation product mentioned above refers to acicular ferrite, which forms in the same temperature range as bainite does in wrought steels. Investigation has led to the identification of acicular ferrite as a variant of bainite but nucleated on inclusions within the austenite grains.

Depending on alloy composition and cooling rate, acicular ferrite can form after allotriomorphic ferrite formation has occurred on the γ/γ boundaries or before this transformation has had an opportunity to begin (*e.g.* in high strength welds). In the case of some steels in which transformation kinetics are fast, research suggests that the presence of allotriomorphic ferrite is essential in order to suppress the nucleation and rapid dominance of bainite at these boundaries (Babu & Bhadeshia, 1991).

Following the acicular ferrite transformation, the remaining austenite can form a variety of 'microphases'. This term refers to martensite, pearlite or retained austenite. The grouping of the acicular ferrite and microphases together, as is done in some welding research papers loses its meaning when considering high strength welds which consist entirely of acicular ferrite and martensite (Bhadeshia & Svensson, 1988). Allotriomorphic ferrite, Widmanstätten ferrite and acicular ferrite are shown together in a weld microstructure in Figure 1.14.

The Role of Inclusions in Microstructure Development

As a result of the deoxidation reactions at high temperatures within the weld pool, particles of non-metallic compounds that do not separate into the slag layer become trapped in the solidifying steel.

During solidification to δ ferrite the inclusions are swept to the δ/δ boundary regions of the cellular front as it progresses. The resulting alignment of the inclusion particles is retained



Figure 1.14 The morphology of allotriomorphic ferrite α , Widmanstätten ferrite α_W and acicular ferrite α_a in a weld deposit

to room temperature even though austenite formation means that the particles are no longer located at grain boundaries in the final microstructure.

In general the presence of foreign bodies in the weld metal affects its homogeneity, which is a crucial factor in determining physical properties. Inclusions in particular act as stress raisers, increasing the chances of crack initiation. However, they are also the sites for the intragranular nucleation of acicular ferrite which is beneficial to weld properties.

It has been shown that in order to optimise their nucleating properties the inclusions must (a) be of the correct chemical composition; (b) be present in sufficient numbers; and (c) have the correct size distribution (Grong & Matlock, 1986).

The exact nature of nucleation at the inclusion surface is not known. It has been found that inclusions having the greatest difference in thermal expansion coefficient with austenite are the most effective nucleants. Also postulated is that nucleating effect might be attributed to (a) the presence of dislocations formed by deformation of the austenite driven by the differential thermal contraction at the inclusion/matrix interface; (b) the interaction of transformation strain of the acicular ferrite particle with the stress field around the inclusion; (c) the presence of the inclusion as an inert heterogeneous nucleation site (Farrar & Harrison, 1987). Chemical reactions at the ferrite/inclusion interface are also possible (Strangwood & Bhadeshia, 1987;

1.5 An Outline of the Weld Fusion Zone Microstructure Model

Utilising phase transformations theory, combined with experimental data, a semi-empirical model has been developed by Bhadeshia and co-workers over recent years, that is capable of some remarkably accurate predictions of weld microstructure.

From the chemical composition of the weld metal its phase diagram and TTT diagram can be calculated. From the welding variables such as process type, heat input and interpass temperature, the cooling behaviour of the weld can be estimated. Combination of isothermal transformation diagrams and cooling curve enables the volume fraction of the phases forming as the weld cools to be calculated

The sequence of reactions in the cooling weld is modelled as follows. Solidification is considered to occur as δ ferrite, and by considering the solute partitioning coefficient k between the ferrite and the liquid at the liquidus temperature the extent of solute segregation at room temperature can be estimated since there is little chance for homogenisation during cooling. Hence the composition of the segregated regions with respect to the element *i* is $k_i x_i$ (Gretoft *et al.* 1986).

It is not possible to estimated the austenite grain size that forms from the ferrite from fundamental theory and so a crude estimation of the transverse mean linear intercept \overline{L} with the grain structure is made by the use of a regression equation.

$$\overline{L}(\mu m) = 64.5 - 445.8(wt\%C) - 139(wt\%Si) - 7.6(wt\%Mn) + 16(heat input kJ mm^{-1})$$

The first phase to form from the austenite is allotriomorphic ferrite. Transformation is assumed to begin when the Scheil approximation sum, applied to the calculated TTT diagram for the solute depleted regions, reaches unity. The time and temperature of this event are designated t_h and T_h respectively. Since boundary decoration by allotriomorphic ferrite is fast compared to growth normal to the interface, the transformation can be approximated as one dimensional carbon controlled growth, and paraequilibrium applies under the fast cooling conditions. The allotriomorph thickness q integrated over the temperature range T_h to T_l is

$$q = \int_{T_h}^{T_l} \left(0.5\alpha_1 t^{-1/2} \right) dt$$

where T_l represents the temperature at which the diffusional and displacive TTT curves cross, t_l being the time at which this happens. The value of α_1 is obtained by solving the equation

$$\frac{2\left(\underline{D_{11}}/\pi\right)^{1/2}\left(x^{\gamma\alpha}-\overline{x}\right)}{x^{\gamma\alpha}-x^{\alpha\gamma}} = \alpha_1 \exp\left\{\frac{\alpha_1^2}{4\underline{D_{11}}}\right\} \operatorname{erfc}\left\{\frac{\alpha_1}{2\underline{D_{11}}^{1/2}}\right\}$$

which relates the mass of partitioned carbon from ferrite to that in the diffusion field ahead of the advancing interface. It is suggested that the major effect of alloying elements on weld metal transformation characteristics is by their effect and the kinetics of allotriomorphic ferrite formation.

The geometry of the grain structure, approximated by hexagonal prisms, relates the volume fraction of allotriomorphic ferrite to the allotriomorph thickness q.

$$V_{\alpha} = \frac{(2q \tan \{30^{\circ}\} (2a - 2q \tan \{30^{\circ}\}))}{a^2}$$

where a is the hexagonal austenite grain side length.

The next phase to form is Widmanstätten ferrite. The lengthening rate G of the plates is constant and can be estimated using the Trivedi theory of pate growth. If growth occurs for a time t_2 then the fraction of Widmanstätten ferrite growing from the austenite grain boundary, which may, or may not be covered with allotriomorphic ferrite is

$$V_{\alpha_W} = C_4 G\left(\frac{2a - 4q \tan\left\{30^\circ\right\}}{2a}\right) t_2^2$$

where the presence of q indicates the effect of previously formed allotriomorphic ferrite on the available volume for Widmanstätten ferrite growth. An important factor in determining the volume fraction of this phase is the term t_2 . If the plate can grow unhindered across and austenite grain in time t_g then t_2 equals this time. If impingement with intragranularly nucleated acicular ferrite occurs after t_c and $t_c < t_g$ then t_2 will equal t_c . It is not possible to evaluate t_c from fundamental principles and so an empirically determined time of 2.011 s is used.

The final microstructural component to be estimated is acicular ferrite which is deduced by difference

$$V_{\alpha_a} = 1 - V_\alpha - V_{\alpha_W} - V_m$$

The volume fraction of microphases V_m can be estimated thermodynamically by equating it to the volume fraction of untransformed austenite given by the paraequilibrium phase diagram, at the M_S temperature.

The microstructure model also predicts the effect of trace elements such as boron on the transformation behaviour of the steel, as well as predicting the chemistry of the non-metallic inclusions in the weld by considering the relative stability of the various inclusion phases that can form, given the composition of the steel.

Attempts have been made to model the relationship between microstructure and properties of welds. This process involves accounting for the solid solution as well as the microstructural strengthening effect of the various alloying elements and has met with reasonable success (Sugden, 1988). It is also of great importance to account for the scatter in toughness seen in weld deposits. This is accounted for in a novel way by considering the cause of such scatter to be the microstructural inhomogeneity of the weld resulting from the presence of more than one phase (Sugden & Bhadeshia, 1989). To refer to this inhomogeneity as entropy is however a mistake, since inhomogeneity implies a low entropy condition.

CHAPTER 2

Mathematical Modelling of Phase Transformations

2.1 Mathematical Modelling of Phase Transformations

The first step in modelling phase transitions in steels is to represent the chemical potential changes occurring in the austenite and ferrite phases as a function of carbon concentration and temperature. For the modelling of paraequilibrium transformation, other alloying elements can be accounted for by their effect on the transitions in pure iron. The free energy of ferrite at temperature T, carbon mole fraction x^{α} is

$$G^{\alpha} = x^{\alpha} \left(\mu_{C}^{0} + RT \ln \{ a_{C}^{\alpha} \} \right) + (1 - x^{\alpha}) \left(\mu_{Fe}^{\alpha 0} + RT \ln \{ a_{Fe}^{\alpha} \} \right)$$
(2.1)

where a_C^{α} and a_{Fe}^{α} refer to the activity of carbon and iron, respectively, in the ferrite. The term μ_C^0 and $\mu_{Fe}^{\alpha 0}$ refer to the chemical potentials of graphite and of pure ferritic iron. Using analogous notation, the free energy of austenite of carbon mole fraction x^{γ} is

$$G^{\gamma} = x^{\gamma} \left(\mu_{C}^{0} + RT \ln \{ a_{C}^{\gamma} \} \right) + (1 - x^{\gamma}) \left(\mu_{Fe}^{\gamma 0} + RT \ln \{ a_{Fe}^{\gamma} \} \right)$$
(2.2)

The activities of carbon and iron in ferrite and austenite are themselves functions of the carbon mole fraction. These quantities can be estimated by use of the statistical thermodynamic theory of Lacher (1937) and Fowler & Guggenheim (1939).

Considering the ferrite phase, the activity of carbon is

$$\ln a_C^{\alpha} \{x^{\alpha}\} = 4 \ln \left[\frac{(9 - 6(2J_{\alpha} + 3)x^{\alpha} + (9 + 16J_{\alpha})(x^{\alpha})^2)^{1/2} - 3 + 5x^{\alpha}}{(9 - 6(2J_{\alpha} + 3)x^{\alpha} + (9 + 16J_{\alpha})(x^{\alpha})^2)^{1/2} + 3 - 5x^{\alpha}} \right]$$
$$+ 3 \ln \left[\frac{3 - 4x^{\alpha}}{x^{\alpha}} \right] + \frac{4w_{\alpha}}{RT} + \frac{\Delta \overline{H}_{\alpha} - \Delta \overline{S}_{\alpha} T}{RT}$$
(2.3)

where J_{α} is given by

$$J_{\alpha} = 1 - \exp\left(\frac{-w_{\alpha}}{RT}\right) \tag{2.4}$$

where w_{α} is the carbon-carbon interaction energy for ferrite and the terms $\Delta \overline{H}_{\alpha}$ and $\Delta \overline{S}_{\alpha}$ are the partial molar enthalpy and non-configurational entropy for solid solution of carbon in ferrite. By applying the Gibbs-Duhem relationship to the expression for the activity of carbon, the activity of iron can also be determined for ferrite. This gives (Hsu & Mou Yiwen, 1984), using analogous notation to the expression for ferrite

$$\ln a_{Fe}^{\alpha}\{x^{\alpha}\} = +9\ln\left[\frac{3(1-x^{\alpha})}{(3-4x^{\alpha})}\right]$$

$$+12\ln\left[\frac{3(1-2J_{\alpha})+(8J_{\alpha}-3)x^{\alpha}-(9-6(2J_{\alpha}+3)x^{\alpha}+(9+16J_{\alpha})(x^{\alpha})^{2})^{1/2}}{2J_{\alpha}(4x^{\alpha}-3)}\right]$$
(2.5)

In the austenite phase the activity of carbon is given by

$$\ln a_C^{\gamma} \{x^{\gamma}\} = 6 \ln \left[\frac{(1 - 2(1 + 2J_{\gamma})x^{\gamma} + (1 + 8J_{\gamma})(x^{\gamma})^2)^{1/2} - 1 + 3x^{\gamma}}{(1 - 2(1 + 2J_{\gamma})x^{\gamma} + (1 + 8J_{\gamma})(x^{\gamma})^2)^{1/2} + 1 - 3x^{\gamma}} \right]$$
$$+ 5 \ln \left[\frac{1 - 2x^{\gamma}}{x^{\gamma}} \right] + \frac{6w_{\gamma}}{RT} + \frac{\Delta \overline{H}_{\gamma} - \Delta \overline{S}_{\gamma} T}{RT}$$
(2.6)

where

$$J_{\gamma} = 1 - \exp\left(\frac{-w_{\gamma}}{RT}\right) \tag{2.7}$$

The activity of iron austenite is then given by

$$\ln a_{Fe}^{\gamma} \{x^{\gamma}\} = 6 \ln \left[\frac{1 - 2J_{\gamma} + (4J_{\gamma} - 1) - (1 - 2(1 + 2J_{\gamma})x^{\gamma} + (1 + 8J_{\gamma})(x^{\gamma})^2)^{1/2}}{2J_{\gamma}(2x^{\gamma} - 1)} \right] + 5 \ln \left[\frac{1 - x^{\gamma}}{1 - 2x^{\gamma}} \right]$$
(2.8)

The thermodynamic data for w_{γ} , $\Delta \overline{H}_{\alpha}$ and $\Delta \overline{H}_{\gamma}$ can be found in the work of Shiflet *et al.* (1978). $\Delta \overline{S}_{\alpha}$ and $\Delta \overline{S}_{\gamma}$ is taken from Lobo *et al.* (1976). The value of w_{α} was obtained by Bhadeshia (1980).

2.1.1 The $\gamma \rightarrow \gamma_1 + \alpha$ Transformation

For the transition of austenite to the equilibrium $\alpha + \gamma$ phase mixture, the free energy change $\Delta G^{\gamma \to \gamma_1 + \alpha}$ is shown diagrammatically in Figure 2.1. The equilibrium ferrite and austenite compositions are $x^{\alpha\gamma}$ and $x^{\gamma\alpha}$ respectively. The value of the free energy change is given by the expression

$$\Delta G^{\gamma \to \gamma_1 + \alpha} = v G^{\alpha} \{T, x^{\alpha \gamma}\} + (1 - v) G^{\gamma} \{T, x^{\gamma \alpha}\} - G^{\gamma} \{T, \overline{x}\}$$

$$= v \left(x^{\alpha \gamma} \left(\mu_C^0 + RT \ln \{a_C^{\alpha}|_{x^{\alpha \gamma}}\} \right) + (1 - x^{\alpha \gamma}) \left(\mu_{Fe}^{\alpha 0} + RT \ln \{a_{Fe}^{\alpha}|_{x^{\alpha \gamma}}\} \right) \right)$$

$$+ (1 - v) \left(x^{\gamma \alpha} \left(\mu_C^0 + RT \ln \{a_C^{\gamma}|_{x^{\gamma \alpha}}\} \right) + (1 - x^{\gamma \alpha}) \left(\mu_{Fe}^{\gamma 0} + RT \ln \{a_{Fe}^{\gamma}|_{x^{\gamma \alpha}}\} \right) \right)$$

$$- \overline{x} \left(\mu_C^0 + RT \ln \{a_C^{\gamma}|_{\overline{x}}\} \right) + (1 - \overline{x}) \left(RT \ln \{a_{Fe}^{\gamma}|_{\overline{x}}\} \right)$$
(2.9)

where

$$v = \frac{\overline{x} - x^{\gamma\alpha}}{x^{\alpha\gamma} - x^{\gamma\alpha}} \tag{2.10}$$

 $a_{Fe}^{\alpha}|_{x^{\alpha\gamma}}$ and $a_{C}^{\alpha}|_{x^{\alpha\gamma}}$ denote the activities of carbon and iron in ferrite of composition $x^{\alpha\gamma}$ respectively. The activities of carbon and iron in austenite at composition $x^{\gamma\alpha}$ are expressed as



Figure 2.1 Free energy change on decomposition of austenite into a two-phase α/γ mixture of equilibrium composition.

 $a_C^{\gamma}|_{x^{\gamma\alpha}}$ and $a_{Fe}^{\gamma}|_{x^{\gamma\alpha}}$. For austenite of bulk alloy composition the activities of carbon and iron are expressed as $a_C^{\gamma}|_{\overline{x}}$ and $a_{Fe}^{\gamma}|_{\overline{x}}$. The resulting free energy change is

$$\Delta G^{\gamma \to \gamma_1 + \alpha} = \left(\mu_{Fe}^{\alpha \, 0} - \mu_{Fe}^{\gamma \, 0} \right) + RT v \left(x^{\alpha \gamma} \ln \left\{ a_C^{\alpha} \right|_{x^{\alpha \gamma}} \right\} + \left(1 - x^{\alpha \gamma} \right) \ln \left\{ a_{Fe}^{\alpha} \right|_{x^{\alpha \gamma}} \right\})$$
$$+ RT \left(1 - v \right) \left(x^{\gamma \alpha} \ln \left\{ a_C^{\gamma} \right|_{x^{\gamma \alpha}} \right\} + \left(1 - x^{\gamma \alpha} \right) \ln \left\{ a_{Fe}^{\gamma} \right|_{x^{\gamma \alpha}} \right\})$$
$$- RT \left(1 - v \right) \left(\overline{x} \ln \left\{ a_C^{\gamma} \right|_{\overline{x}} \right\} + \left(1 - \overline{x} \right) \ln \left\{ a_{Fe}^{\gamma} \right|_{\overline{x}} \right\})$$
(2.11)

This value can then be calculated by substituting in the activity expressions $a_C^{\alpha}|_{x^{\alpha\gamma}}$, $a_{Fe}^{\alpha}|_{x^{\alpha\gamma}}$, $a_C^{\gamma}|_{x^{\gamma\alpha}}$, $a_{Fe}^{\gamma}|_{x^{\gamma\alpha}}$, $a_{Fe}^{\gamma}|_{\overline{x}}$.

2.1.2 The Free Energy Change on Nucleation

During nucleation only a very small amount of precipitate phase is formed, and the composition of the matrix hardly changes. The most likely nucleus composition will be that which gives the maximum free energy change under these conditions, since this nucleus will have the greatest chance of overcoming the activation barrier to nucleation.

For negligible matrix composition change the free energy change per mole of precipitate is given by the separation of the tangent to the austenite curve, at the bulk composition \overline{x} with



Figure 2.2 Choice of nucleus composition in order to maximise the free energy change on formation of a small amount of precipitate phase. The driving force per mole of nucleus is given by the separation of the ferrite curve from the tangent to the austenite curve at the bulk composition.

the ferrite curve at the composition of the precipitate. The maximum value of the free energy change will be for the ferrite composition x_m where a parallel tangent touches the ferrite curve, as is shown in Figure 2.2. The condition can be described as

$$\left. \frac{\partial G^{\alpha}}{\partial x} \right|_{x_m} = \left. \frac{\partial G^{\gamma}}{\partial x} \right|_{\overline{x}} \tag{2.12}$$

This equation can be obtained by differentiating the free energy expressions above, and solving for x_m numerically. The maximum free energy change ΔG_m is then

$$\Delta G_m = RT \ln \left\{ \frac{a_C^{\gamma}|_{\overline{x}}}{a_C^{\alpha}|_{x_m}} \right\}$$
(2.13)

2.1.3 Thermodynamics of Nucleation of Bainite and Widmanstätten Ferrite

Theory states that nucleation of Widmanstätten ferrite and bainite occurs when ΔG_m is greater than a critical (temperature dependent) value G_N .

$$G_N = 3.636T - 2540 \text{ J mol}^{-1}$$
 (2.14)



Figure 2.3 Widmanstätten ferrite formation is impossible at intermediate temperatures where the driving force ΔG_m is less than the critical value given by the G_N curve. The lower C-curve then seperates into regions giving Widmanstätten ferrite and bainite.

It has been calculated (Svensson & Bhadeshia, 1988) that in the case of some weld metals the ΔG_m curve intersects with G_N at two temperatures, resulting in a region at intermediate temperature where nucleation is impossible. This case is shown in Figure 2.3. For the cases in which nucleation is possible, in the upper region Widmanstätten ferrite forms, whereas in the lower region nucleation leads to bainite formation.

2.1.4 Thermodynamics of Growth of Bainite

For growth by a diffusionless transformation it is necessary for there to be a negative free energy change for the formation of α of the same composition as the γ matrix. Because of the elastic stored energy of bainite, an additional 400 J mol⁻¹ is also required. The locus of temperatures on the phase diagram at which the change from austenite to ferrite of the same composition becomes possible is called the T_0 curve. For strained ferrite, as in bainite, the modified curve is designated T'_0 .

The effect of this requirement is to shift the free energy curve of ferrite relative to that of austenite. This is represented in Figure 2.4 which also shows the T_0 and T'_0 curves where austenite has the same free energy as unstrained and strained ferrite respectively.



Figure 2.4 Free energy curves for ferrite and austenite, and T_0 curve locus.

As the temperature decreases it first becomes thermodynamically possible to form bainite when the temperature lies below the T'_0 curve for the given composition, as long as nucleation is also possible. Also, as isothermal transformation proceeds, when the untransformed austenite becomes carbon-enriched to such an extent that the T'_0 curve is reached, transformation must cease.

2.1.5 Modelling of Martensitic Nucleation

Since bainite is thought to be a product of diffusionless displacive reaction, with excess carbon rejected into the residual austenite subsequent to transformation, it can be considered similar to martensite. The essential difference between the phases results from the fact that martensite nucleates without diffusion of carbon.

The martensitic transformation occurs by the motion of a glissile interface between the ferrite and austenite. The dislocations in such an interface cannot have their Burgers vectors in the interface plane. If this condition is satisfied, the interface can advance without the need for diffusion.

A stacking fault on closest packed planes forms a thin layer of ferrite within the parent austenite. If such a fault has an n planes, each of area A, and the molar density of atoms on

the planes is ρ then the total fault energy W is

$$W = n\rho A (\Delta G^{\text{chem}} + E^{\text{str}}) + 2\sigma \{n\}$$
(2.15)

where ΔG^{chem} is the molar chemical free energy difference between the two phases, E^{str} is the molar strain energy and σ is the surface energy per unit area of the particle.

By applying the criterion that the barrier to growth is the flow stress of the dislocations in the glissile interface between the matrix and embryo, an expression is formed defining the critical size of particle. If the dislocations require a stress τ_0 for motion, the force per unit length necessary to separate the dislocations, each of Burgers vector **b** is

$$n\tau_0 b$$
 (2.16)

A fault of energy W will exert a force -W on such an array. The fault will therefore exert sufficient force when

$$n^* \rho A (\Delta G^{\text{chem}} + E^{\text{str}}) + \tau_0 b = -2\sigma \tag{2.17}$$

where n^* is the number of planes in the critical nucleus. If the flow stress of the dislocations has an athermal component as well as a component dependent on temperature, the isothermal and thermal type of martensitic transformations can be rationalised. The activation energy of dislocation motion under an applied stress τ can be represented as

$$Q = Q_0 + (\tau - \tau_{\mu})v^* \tag{2.18}$$

where τ_{μ} is the athermal component of the flow stress and v^* is the activation volume of the nucleus.

If there exists a maximum and minimum rate at which the interface can advance, \dot{r}_{max} and \dot{r}_{min} respectively, depending on how the quantities $nb\tau_0$ and W vary with temperature, different steels can fall into the isothermal or athermal transformation regimes. This is shown in Figure 2.5.

As temperature increases the magnitude of the term $-nb\tau_0$ changes until it reaches its athermal value $nb\tau_{\mu}$. For different materials the variation of W is shown schematically in the figure. If the curves cross at a temperature where the flow stress has its athermal value then martensitic transformation will be athermal since the extent of transformation then depends only on the number of nuclei that have been activated. If transformation becomes possible in the regime where flow stress is temperature dependent the activation energy is dependent on the driving force and isothermal transformation will occur. C-curve type kinetics are also expected, since, as shown in Figure 2.5, there is a temperature at which the chosen value of \dot{r} is at a maximum.



Figure 2.5 Isothermal and athermal martensite nucleation regimes.

Under isothermal transformation conditions the activation energy for nucleation then becomes

$$Q = Q_0 + \left(\tau_\mu + \frac{\rho A E^{str}}{b} + \frac{2\sigma}{nb}\right)v^* + \left(\frac{\rho v^*}{b}\right)\Delta G^{\text{chem}}$$
(2.19)

2.1.6 TTT Diagram Theory and Application

Extensively used in designing heat treatments for steels, isothermal transformation diagrams, or Time-Temperature-Transformation (TTT) diagrams represent the time necessary for a reaction to initiate at a given temperature. The diagrams are particularly useful in identifying the temperature regions in which different transformation products form. This identification becomes increasingly easy as the substitutional alloying element content of the steel is increased to such an extent that reconstructive and displacive reactions are separated into two distinct regions, each possessing its own characteristic C-curve. The typical effect of increasing alloying elements concentration is shown in Figure 2.6.

In a model for predicting steel microstructure it is of great importance to be able to predict the onset time for a given transformation. For isothermal transformation the incubation time τ corresponds to the time taken for a detectable amount of the precipitate phase to form. For continuous cooling experiments, it it possible to predict the onset time and temperature from knowledge of the TTT diagram, using the Scheil approximation. The cooling curve is first





Figure 2.6 The effect on a typical isothermal transformation diagram of increasing the alloying element concentration in the steel. a) low substitutional alloy content b) increased substitutional alloy content.

approximated as a series of isothermal step treatments, the i^{th} step at T_i being of length t_i . Transformation is calculated to begin when the sum

$$\sum_{i=1}^{i} t_i / \tau_i = 1 \tag{2.20}$$

where τ_i represents the incubation period at T_i . Mathematical modelling of the incubation time period is therefore of great use. A successful model, based on the semi-empirical analysis of existing TTT diagrams was published by Bhadeshia (1982). The incubation time is considered to follow a relationship analogous to that which the steady-state nucleation incubation time follows for reconstructive transformation (Russell 1968, 1969) *i.e.*

$$\tau \propto \frac{T}{\left(\Delta G_m^v\right)^p D} \tag{2.21}$$

where ΔG_m^v represents the maximum volume free energy change on nucleation of a small amount of precipitate, D represents the appropriate diffusion coefficient, T the absolute temperature and p a parameter linked to nature of the nucleus.

For prediction of steel TTT diagrams there is insufficient knowledge concerning the nature of the nucleus to allow fundamental choices of p and D, so these parameters were derived merely by curve fitting. D is temperature related in the following way

$$D \propto \exp\left\{S/R\right\} \exp\left\{-Q/RT\right\}$$
(2.22)

where S and Q are the diffusion entropy and enthalpy respectively, which are themselves temperature dependent. The resulting equation used to fit the theory to the experimental values of τ has the form

$$\ln\left\{\frac{\tau\left(\Delta G_m\right)^p}{T^z}\right\} = \frac{Q'}{RT} + C_4 \tag{2.23}$$

where the term z accounts for the temperature dependence of diffusion enthalpy and entropy. Parameters p and z and C_4 are then optimised in order to produce the maximum correlation with the experimental data.

The results of this semi-empirical analysis are accurate, especially when combined with the other predictable properties of TTT diagrams. The flat top appearance of the lower C– curve when nucleation of displacive transformations first becomes possible, at temperatures below which the thermodynamic growth criterion of bainite has been satisfied, is reproduced by cutting off the lower C–curve at this temperature. The lower curve is also cut off at the M_S temperature which can be predicted thermodynamically (Bhadeshia 1981a, 1981b).

2.1.7 Kinetics of Allotriomorphic Ferrite Formation

Diffusion-controlled growth means that the rate of interface motion is governed by the transport of atoms to and from the interface. In all cases experimental evidence supports the view that allotriomorphic ferrite forms by diffusion-controlled growth.



Figure 2.7 Composition profiles for diffusion controlled growth of ferrite in a plain carbon steel.

In plain carbon steels of bulk carbon composition \overline{x} , with ferrite and austenite interface compositions $x^{\alpha\gamma}$ and $x^{\gamma\alpha}$ respectively, with an advancing interface of position Z, the composition profile in the austenite is shown in Figure 2.7. From dimensional arguments (Christian 1975) it is argued that the interface position for diffusional growth has the form

$$Z = \alpha_1 t^{1/2}$$
(2.24)

where Z is the position of the interface on the z axis. The constant of proportionality α_1 is known as the parabolic thickening constant.

At the ferrite/austenite interface Fick's law states that

$$\frac{\partial x_1}{\partial t} = \frac{\partial}{\partial z} \left(D_{11} \left\{ x_1 \right\} \frac{\partial x_1}{\partial z} \right)$$
(2.25)

where x_1 refers to the mole fraction of carbon, D_{11} is the diffusion coefficient of carbon in austenite. Mass balance considerations give the following relationship

$$dZ \left(x^{\gamma \alpha} - x^{\alpha \gamma} \right) = D_{11} \left| \frac{\partial x_1}{\partial z} \right|_{z=Z} dt$$
(2.26)

where $x^{\alpha\gamma}$ and $x^{\gamma\alpha}$ are the interface compositions of ferrite and austenite respectively. The

parabolic rate constant to be related to the interface conditions by the equation

$$\frac{\alpha_1 t^{-1/2}}{2} \left(x^{\gamma \alpha} - x^{\alpha \gamma} \right) = D_{11} \left| \frac{\partial x_1}{\partial z} \right|_{z=Z}$$
(2.27)

In general the diffusion coefficient is concentration dependent and so assumptions about the form of the variation have to be made. A useful approximation is to substitute the weighted average diffusivity \underline{D}_{11} for the diffusion coefficient of carbon. This enables analytical solutions to the differential equations to be obtained.

$$\underline{D_{11}} = \int_{\overline{x}}^{x^{\gamma\alpha}} \frac{D_{11}\{x'\}\,dx'}{(x^{\gamma\alpha} - \overline{x})} \tag{2.28}$$

Alloy Steels: Local Equilibrium Growth

In Fe–X–C alloys, X being a substitutional alloying element, an added complication of diffusion of the substitutional alloying element arises. In general, the diffusivities of the interstitial and substitutional species are vastly different. For equilibrium to be maintained at the interface, and for the transport requirements of all atoms from the interface to be satisfied simultaneously *i.e.* the interface velocity $V_{\rm int}$ must satisfy the simultaneous equations

$$(x_1^{\gamma\alpha} - x_1^{\alpha\gamma}) V_{\text{int}} = D_{11} \nabla x_1$$
(2.29)

and

$$(x_2^{\gamma\alpha} - x_2^{\alpha\gamma}) V_{\rm int} = D_{22} \nabla x_2 \tag{2.30}$$

where x_1 and x_2 are the concentrations of carbon and X respectively, with D_{22} being the diffusion coefficient of the substitutional solute. The superscripts $\alpha\gamma$ and $\gamma\alpha$ denote the *interface* values of x_1 and x_2 in the ferrite and the austenite respectively.

Because $D_{11} \gg D_{22}$ the bulk alloy equilibrium compositions cannot be adopted by the interface whilst simultaneously satisfying the flux equations for carbon and X. Modified values are adopted instead, bringing the transport of both species to the required level whilst maintaining local equilibrium at the boundary. For such conditions the growth still follows parabolic interface advancement.

$$Z = \alpha_1 t^{1/2} = \eta_1 \left(D_{11} t \right)^{1/2} = \eta_2 \left(D_{22} t \right)^{1/2}$$
(2.31)

where η_1 and η_2 are growth constants. The interface compositions can be calculated since only one of $x^{\alpha\gamma}$, $x_2^{\alpha\gamma}$, $x^{\gamma\alpha}$, $x_2^{\gamma\alpha}$ are independent (Coates 1973).

Alloy Steels: Paraequilibrium Growth

In a ternary alloy, if the mole fractions of carbon, a substitutional alloying element and iron are x, x_2 and x_3 respectively, under paraequilibrium conditions the ratio

$$\frac{x_2}{x_3}$$

is constant across the α/γ boundary during ferrite growth. Carbon adopts paraequilibrium interface compositions giving it equal chemical potential in both phases across the interface.

The transition from local to paraequilibrium is thought to occur at interface velocities of the kind that would involve the concentration spike associated with the substitutional alloy element during NPLE growth becoming small with respect to interatomic distances, in which case its physical significance is gone. It has been suggested that, if z_{2d} represent the extent of the diffusion field of the substitutional alloy element the the transition from local to paraequilibrium occurs when (Coates, 1973)

$$z_{2d} = \frac{2D_{22}}{V_{\text{int}}} \tag{2.32}$$

2.2 Bainite Overall Transformation Kinetics Model

This model was proposed by Bhadeshia (1982b) in order to incorporate the then recentlydeveloped theories on the displacive nucleation and growth of bainite into a self-consistent model. Since modifications are made in this work, in order to correct certain errors in the original model, it is necessary to present the original theory in detail.

Thermodynamically it is impossible to form bainite if the carbon concentration of the austenite is greater than or equal to the $x_{T'_0}$ composition (Bhadeshia & Edmonds, 1980). Therefore, at a given temperature below B_S there exists a maximum possible ferrite volume fraction θ , where

$$\theta = \frac{x_{T_0'} - \bar{x}}{x_{T_0'} - x^{\alpha}}$$
(2.33)

where $x_{T'_0}$ and therefore θ are functions of temperature. It is then convenient to define a normalised volume fraction ξ

$$\xi = v/\theta \tag{2.34}$$

where v is the actual ferrite volume fraction, θ being the limiting volume fraction.

For consistency with martensite nucleation theory, nucleation of bainite is considered to have an activation energy proportional to the nucleation driving force ΔG_m . *i.e.*

$$I = C_1 \exp\left\{\left(\frac{C_2 - C_3 \Delta G_m}{RT}\right)\right\}$$
(2.35)

where C_1 , C_2 and C_3 are constants. At the W_S temperature, when ΔG_m equals G_N (Bhadeshia 1981a)

$$I = I_{W_S} \exp\left\{-\frac{C_2 \Delta T}{RTW_S} - \frac{C_3}{R} \left(\frac{\Delta G_m}{T} - \frac{G_N}{W_S}\right)\right\}$$
(2.36)

 ΔG_m will vary as the reaction proceeds because the carbon partitioned from the bainitic ferrite will enrich the untransformed austenite. The effect of such enrichment on ΔG_m is modelled as a linear function of the extent of reaction in the following way

$$\Delta G_m = \Delta G_m^{\ 0} \left(1 - (C_4/C_3)\theta\xi \right)$$
(2.37)

with C_4 being a constant, hence

$$I = I_{W_S} \exp\left\{-\frac{C_2 \Delta T}{RTW_S} - \frac{C_3}{R} \left(\frac{\Delta G_m^{\ 0}}{T} - \frac{G_N}{W_S}\right)\right\} \exp\left\{\frac{\Delta G_m^{\ 0} C_4 \theta\xi}{RT}\right\}$$
(2.38)

Bainite is known to exhibit autocatalysis, where the presence of previously formed ferrite increases the nucleation rate of further plates (Bhadeshia & Christian, 1990). This can be approximated as a linear increase in nucleation site density with true volume fraction *i.e.*

$$I_{W_S} = I_0 \left(+\beta\theta\xi \right) \tag{2.39}$$

where β is the auto-catalysis constant. Representing

$$\Gamma = \frac{\Delta G_m^{\ 0} C_4 \theta}{RT} \tag{2.40}$$

this gives

$$I = I_0 \exp\left\{-\frac{C_2 \Delta T}{RTW_S} - \frac{C_3}{R} \left(\frac{\Delta G_m^0}{T} - \frac{G_N}{W_S}\right)\right\} \exp\left\{\Gamma\xi\right\}$$
(2.41)

Forming a differential equation according to the theories of Johnson, Mehl & Avrami, modified for the case of transformation to a limiting volume fraction (Christian 1975).

$$\frac{\theta d\xi}{dt} = uI\left\{\xi\right\}\left(1-\xi\right) \tag{2.42}$$

where u is the average volume of a bainitic sub–unit. The equation can be separated into partial fractions

$$\int_{0}^{\xi} \frac{Ad\xi}{(1-\xi)} + \int_{0}^{\xi} \frac{Bd\xi}{(1+\beta\theta\xi)} + \int_{0}^{\xi} C \exp\left\{-\Gamma\xi\right\} d\xi$$
$$= \frac{uI_{0}}{\theta} \exp\left\{-\frac{C_{2}\Delta T}{RTW_{S}} - \frac{C_{3}}{R}\left(\frac{\Delta G_{m}^{\ 0}}{T} - \frac{G_{N}}{W_{S}}\right)\right\} t \qquad (2.43)$$

where A, B and C are the constants arising from the separation of the equation into partial fractions.

$$A = \frac{\exp\left\{\Gamma\right\}}{(1+\beta\theta)} \tag{2.44}$$

$$C = \frac{1 - e^{\Gamma/\beta} \left(1 - 1/\beta + A/\beta + A\theta\right)}{\left(1 - 1/\beta\right) \left(1 + \theta - e^{\Gamma/\beta}\right)}$$
(2.45)

$$B = 1 - C - A \tag{2.46}$$

The equation can be solved analytically giving the solution

$$t = \frac{\theta \left(-A \ln \{1 - \xi\} + (B/\beta\theta) \ln \{1 + \beta\theta\xi\} + (C/\Gamma) \left(1 - e^{-\Gamma\xi}\right) \right)}{u I_0 \exp \left\{ -\frac{C_2 \Delta T}{RTW_S} - \frac{C_3}{R} \left(\frac{\Delta G_m}{T} - \frac{G_N}{W_S} \right) \right\}}$$
(2.47)

where t represents the time taken to reached a normalised volume fraction ξ at a temperature T.

By optimisation of the fit between the theory and data from dilatometric transformation and three high-silicon steels the constants were evaluated as

$$\beta = 200 \tag{2.48}$$

$$uI_0 = 1.234 \times 10^{-4} \mathrm{s}^{-1} \tag{2.49}$$

$$C_2 = 29710 \text{ J mol}^{-1} \tag{2.50}$$

$$C_3 = 3.769$$
 (2.51)

$$C_4 = 11$$
 (2.52)

This model was shown to give better agreement between predicted and experimental values of the reaction time t than conventional Avrami-type expressions for steels containing sufficient silicon to prevent other reactions, such as carbide precipitation, from interfering with the bainite transformation (Bhadeshia 1982b). The model, however, makes no attempt to model the growth of the ferrite plates, transformation is assumed to occur by the repeated nucleation of plates which appear from the matrix fully formed.

CHAPTER 3

A Modified Bainite Transformation Kinetics Model

3.1 Introduction

The earlier model for the overall transformation kinetics of bainite is corrected and modified here to be consistent with known details of the mechanisms of bainitic nucleation and growth. A comparison with published experimental data shows that the model is capable of accurately representing the development of transformation as a function of alloy chemistry and temperature.

There is currently a large increase in the demand for bainitic steels, cast irons and weld deposits for a wide variety of applications ranging from rail steels to accelerated cooled low-carbon steels for structural engineering (Bhadeshia, 1989; Edmonds & Cochrane, 1990). The research effort backing these developments could benefit greatly from kinetic theory capable of predicting the bainitic microstructures as a function of alloy chemistry and thermomechanical treatment.

The problem is complicated by the fact that there are several microstructural scales to consider (Figure 3.1). The transformation usually begins at the austenite grain surfaces with the nucleation and growth of individual platelets of ferrite. The displacements that occur during growth represent a shape change which is an invariant-plane strain (IPS) with a large shear component (Ko & Cottrell, 1952). The growth of the platelet is stifled by the dislocation debris created as the IPS shape change is plastically accommodated (Bhadeshia & Edmonds, 1979, 1980). The platelets thus grow to a limited size which is usually smaller than the austenite grain size. Further transformation occurs by the formation of new, parallel platelets in clusters known as sheaves; the platelets are therefore called the *sub-units* of the sheaf (Heheman, 1970).

It is believed that the sub-units grow without diffusion, but that any excess carbon in the ferrite is soon afterwards partitioned into the residual austenite (Christian & Edmonds, 1984; Bhadeshia & Christian, 1990). The indications are that the time required to grow a sub-unit is small relative to that needed to nucleate successive sub-units (Bhadeshia, 1984; Ali & Bhadeshia, 1989). The growth rate of individual sub-units (Bhadeshia, 1984) is known to be much faster than the lengthening rate for sheaves (Bhadeshia & Christian, 1990; Ali & Bhadeshia, 1989; Goodenow, Matas & Hehemann, 1963; Speich & Cohen, 1960; Rao & Winchell, 1967).

The overall transformation kinetics include the simultaneous growth and impingement of many different sheaves. A further complication is that carbide precipitation may eventually occur from the carbon-enriched residual austenite, or in the case of lower bainite, from the



Figure 3.1 Schematic illustration of the variety of stages in the development of a bainitic microstructure.

supersaturated ferrite. Carbide precipitation is not addressed in this study, which is confined to situations where the use of alloying additions such as silicon prevent such precipitation. Fortunately, it turns out that the vast majority of bainitic steels which are being actively considered for major applications do not involve carbide precipitation.

The purpose of the work presented here was to develop a model for the overall transformation kinetics, based on the mechanism of the bainite transformation. Such a model was last attempted by Bhadeshia (1982b), but as will be seen in the next section, it contains a number of important discrepancies.

3.2 Problems with the Earlier Theory

In steels containing a relatively large concentration of silicon (> 1.5 wt.%), the precipitation of carbides can be suppressed, especially when the transformation temperature is in the upper bainite range. We have noted that bainitic ferrite sub-units grow without diffusion, but that any excess carbon is soon afterwards partitioned into the residual austenite. This makes it more difficult for subsequent sub-units to grow as the austenite becomes stabilised by its increased carbon concentration. The maximum extent to which the bainite reaction can proceed is therefore determined by the composition of the residual austenite. Bainite growth must cease when the free energies of austenite and ferrite of identical composition become equal. The locus of all points on a temperature/carbon concentration plot, where austenite and ferrite of identical chemistry have equal free energies, is called the T_0 curve; when this is modified to allow for bainite's stored energy of some 400 J mol⁻¹ (Bhadeshia & Edmonds 1980; Bhadeshia & Christian, 1990), the locus becomes the T'_0 curve. Thus, the diffusionless growth of bainitic ferrite becomes impossible when the carbon concentration of the residual austenite reaches the T'_0 concentration. This maximum volume fraction is termed θ . The normalised volume fraction ξ is then defined as

$$\xi = v/\theta \tag{3.1}$$

where v is the actual volume fraction of bainitic ferrite.

The activation energy for the nucleation of bainite is known to be directly proportional to the driving force for transformation (Magee, 1970). This is consistent with the theory for martensite nucleation (Magee, 1970; Olson & Cohen 1976), although it is a requirement that carbon must partition into the austenite during bainite nucleation (Bhadeshia, 1981a). The nucleation mechanism of Widmanstätten ferrite and bainite is considered to be identical; a potential nucleus can develop into either phase depending on whether or not an adequate driving force is available for the growth of bainite at the transformation temperature concerned. On this basis, it is possible to define a universal nucleation function of temperature, G_N , which is applicable to all steels. In a given steel, nucleation first becomes possible at a detectable rate below a temperature W_S (the Widmanstätten ferrite-start temperature), at which magnitude of the maximum nucleation free energy change ΔG_m for the steel exceeds that given by G_N (Bhadeshia, 1981a, 1982a; Ali & Bhadeshia, 1990).

According to the original overall transformation kinetics theory developed by Bhadeshia (1982b), the nucleation rate of ferrite per unit volume I, at any temperature T, can be expressed as a multiple of the nucleation rate at the W_S temperature, I_{W_S} :

$$I = I_{W_S} \exp\left\{-\frac{C_2 \Delta T}{RTW_S} - \frac{C_3}{R} \left(\frac{\Delta G_m}{T} - \frac{G_N}{W_S}\right)\right\}$$
(3.2)

where ΔG_m represents the maximum possible free energy change on nucleation, and G_N is the value of the universal curve representing the minimum necessary free energy change for displacive nucleation of ferrite, at the W_S temperature. C_2 and C_3 are empirical constants. ΔG_m is a function of the volume fraction of ferrite, since carbon enrichment of the untransformed austenite will lower the magnitude of the free energy change as the volume fraction of ferrite increases. This effect is modelled as

$$\Delta G_m = \Delta G_m^0 \left(1 - C_4 \theta \xi / C_3 \right) \tag{3.3}$$

where ΔG_m^{0} is the initial value of ΔG_m , and C_4 is an empirical constant.

The effect of autocatalysis *i.e.* the increase in number density of nucleation sites as the volume fraction of ferrite increases is modelled as

$$I_{W_S} = I_0 \left(1 + \beta \theta \xi \right) \tag{3.4}$$

where β is the empirical autocatalysis constant.

At the onset of transformation, the increment dv of volume fraction of ferrite that forms between times t and t + dt is given by

$$dv = \theta d\xi = I u dt \tag{3.5}$$

where u is the volume of a bainitic sub-unit and I is the nucleation rate per unit volume.

At later stages in the transformation, since the volume of austenite available for transformation will have decreased, it is necessary to consider the increment in the 'extended volume' dv_e (Christian, 1975), which accounts for the formation of 'phantom' nuclei within regions of ferrite already transformed. This enables the use of the nucleation rate of bainite per unit volume of austenite, despite the fact that the volume of austenite is changing, provided that the extended volume increment is related to the real volume increment. This is done in the following way

$$dv = (1 - \xi)dv_e \tag{3.6}$$

where

$$dv_e = Iudt \tag{3.7}$$

which gives

$$\theta d\xi = (1 - \xi) I u dt \tag{3.8}$$

On substituting the expressions for the nucleation rate of bainite this gives

$$\theta \frac{d\xi}{dt} = uI_0(1-\xi)(1+\beta\theta\xi) \exp\left\{\Gamma\xi\right\} \exp\left\{-\frac{C_2\Delta T}{RTW_S} - \frac{C_3}{R}\left(\frac{\Delta G_m^0}{T} - \frac{G_N}{W_S}\right)\right\}$$
(3.9)

where u is the average volume of a single sub-unit, and

$$\Gamma = \frac{C_4 \Delta G_m^{\ 0}}{RT} \tag{3.10}$$

By separating the variables the equation can be integrated

$$\int_{0}^{\xi} \frac{Ad\xi}{(1-\xi)} + \int_{0}^{\xi} \frac{Bd\xi}{(1+\beta\theta\xi)} + C \int_{0}^{\xi} \exp\left\{-\Gamma\xi\right\} d\xi$$
$$= \frac{uI_{0}}{\theta} \exp\left\{-\frac{C_{2}\Delta T}{RTW_{S}} - \frac{C_{3}}{R} \left(\frac{\Delta G_{m}^{\ 0}}{T} - \frac{G_{N}}{W_{S}}\right)\right\} \int_{0}^{t} dt \qquad (3.11)$$

where A, B and C are constants arising from the separation of the differential equation into partial fractions. ΔT is defined as $T - W_S$.

An analytical solution (not presented in the original model) is obtained giving the time t taken to form a normalised volume fraction ξ at the reaction temperature T.

$$t = \frac{\theta \left(-A \ln \left\{1-\xi\right\} + \left(B/\beta \theta\right) \ln \left\{1+\beta \theta \xi\right\} + \left(C/\Gamma\right) \left(1-e^{-\Gamma \xi}\right)\right)}{u I_0 \exp \left\{-\frac{C_2 \Delta T}{RT W_S} - \frac{C_3}{R} \left(\frac{\Delta G_m^0}{T} - \frac{G_N}{W_S}\right)\right\}}$$
(3.12)

After optimisation of the model, the best fit values of the empirical constants were found to be (Bhadeshia, 1982b)

$$uI_0 = 1.234 \times 10^{-4} s^{-1}$$
 $C_2 = 27910 \text{ J mol}^{-1}$ $C_3 = 3.679$
 $C_4 = 11$ $\beta = 200$

The present studies began with the use of this model as a means to the prediction of weld metal microstructures, but it was soon realised that there are certain important errors.

3.2.1 Prediction Errors

A thorough assessment of the model was made, using thermodynamic parameters and theory (necessary to calculate ΔG_m , for example) described when the model was first proposed (Bhadeshia, 1982b). As is shown in Figure 3.2 the original model incorrectly predicts that, at the same transformation temperature, a steel with a high manganese content will transform at a *faster* rate than a more lightly alloyed steel. This prediction is contrary to experience. Table 3.1 gives the compositions of the steels used for the comparison calculation, which was performed for a reaction temperature of 470°C. This temperature was calculated to lie between the bainite–start and martensite–start temperatures for both alloys. The compositions were chosen to be consistent with the welding alloys that are currently being investigated. The values of ΔG_m^0 and G_N and W_S together with the predicted B_S and M_S were calculated using theory outlined by Bhadeshia (1981a).

The model also predicted for all steels that there was a deceleration in transformation rate as the undercooling below W_S increased. An example is given in Figure 3.3 which shows the calculated transformation curves for the isothermal formation of bainite in 300 M steel (composition given in Table 3.2) at a variety of temperatures within the bainite transformation range. The initial reaction rate is predicted to decrease as the isothermal transformation temperature decreases. This is in spite of the fact that driving force increases as temperature decreases. The calculations also contradict experimental data for 300 M, discussed later in this chapter, which show the opposite trend.

A	lloy	С	Si	Mn	Ni	Mo	\mathbf{Cr}	$B_S/^{\circ}\mathrm{C}$	$M_S/^{\circ}\mathrm{C}$
Ste	eel 1	0.06	0.5	2.0	2.0	0.4	0.6	478	406
Ste	eel 2	0.06	0.5	1.0	2.0	0.4	0.6	565	455

Table 3.1 Steel compositions (wt %) and calculated M_S and B_S temperatures used for comparison of predicted reaction rates.



Figure 3.2 The relative reaction rates of a high manganese and a low manganese steel, as predicted by the original bainite transformation kinetics model (Bhadeshia, 1982b). The steel compositions are given in Table 3.1.

3.2.2 Theoretical problems

A key assumption used in the derivation of the universal nucleation function G_N was that at the highest temperature at which ferrite can nucleate by a displacive mechanism (*i.e.* W_S), all steels should have an identical nucleation rate (Bhadeshia, 1981a). The original bainite kinetics model (Bhadeshia, 1982b) is not, in general, consistent with this assumption. This can be shown by comparing the nucleation rates of two steels, A and B, at their W_S temperatures, W_{SA} and W_{SB} respectively. The G_N function represents the minimum driving force necessary to initiate nucleation of ferrite by a displacive mechanism. It is found to be a linear function of temperature (Bhadeshia, 1981a). At the W_S temperature, ΔG_N is given by

$$G_N = pW_S - r \tag{3.13}$$



Figure 3.3 Predicted isothermal transformation curves for 300 M steel (Fe-0.44C-1.74Si-0.67Mn-1.85Ni-0.83Mo-0.39Cr-0.09V) calculated using the original bainite transformation kinetics model (Bhadeshia, 1982b). The curves show that the initial reaction rate is predicted to decrease as the temperature decreases.

where p and r are both positive constants. If G_{NA} and G_{NB} represent the values of G_N at W_{SA} and W_{SB} respectively then

$$G_{NA} = pW_{SA} - r \tag{3.14}$$

and

$$G_{NB} = pW_{SB} - r \tag{3.15}$$

where (Ali & Bhadeshia, 1990)

p = 3.6375 $r = 2540 \text{ J mol}^{-1}$

It follows from equation 3.2, that the ratio of nucleation rates in the two steels at their respective W_S temperatures is given by:

$$\frac{I_A}{I_B} = \exp\left\{-\frac{(C_2 - C_3 r)(W_{SB} - W_{SA})}{RW_{SA}W_{SB}}\right\}$$
(3.16)

From this equation it can be seen that unless

$$C_2 = C_3 r \tag{3.17}$$

different steels will not have the same nucleation rate at their W_S temperature. The values of the terms derived for the original theory (Bhadeshia, 1982b) are

$$C_2 = 27910 \text{ J mol}^{-1}$$
 $C_3 = 3.679$ $r = 2540 \text{ J mol}^{-1}$

which clearly do not satisfy this condition.

A further difficulty was also identified in the modelling of the effect of carbon enrichment of untransformed austenite on the $\gamma \rightarrow \alpha$ free energy change *i.e.*

$$\Delta G_m = \Delta G_m^0 \left(1 - C_4 \theta \xi / C_3 \right) \tag{3.18}$$

with the value of C_4/C_3 equal to 2.98. This equation predicts that the value of ΔG_m will be positive after a volume fraction of bainite of 0.34 has formed, regardless of temperature or alloy chemistry.

Bainite is observed to grow until the carbon content of the untransformed austenite reaches the value given by the T'_0 for the steel. The limiting volume fraction of bainite is therefore a function of temperature and alloy chemistry. It is not therefore reasonable for transformation to cease when a volume fraction of 0.34 is achieved. Indeed, the isothermal transformation data used for the investigation of the original model shows many cases where the volume fractions far greater than 0.34. This can be seen in Figures 3.5–3.7, which show the data for the steels Fe–Mn–Si–C, Fe–Ni–Si–C and 300 M respectively (Bhadeshia, 1982b).

3.3 Development of a New Model

3.3.1 The Nucleation Rate at W_S

To ensure that the activation energy for nucleation remains directly proportional to ΔG_m (Bhadeshia, 1982b), and imposing the condition that the nucleation rate at W_S is constant for all steels, the expression for the nucleation rate of bainite is modified to become

$$I = K_1 \exp\left\{-\frac{K_2}{RT} - \frac{K_2 \Delta G_m}{rRT}\right\}$$
(3.19)

where K_1 and K_2 are constants, denoted by the letter K in order to avoid confusion with the constants of the original theory. K_1 represents the number density of potential sites for nucleation. At W_S the expression becomes

$$I = K_1 \tag{3.20}$$

regardless of the alloy composition.

3.3.2 The Effect of Carbon Partitioning on Free Energy Change

As transformation proceeds it becomes necessary to account for the decrease in driving force due to the carbon-enrichment of untransformed austenite. The effect of auto-catalysis also becomes important.

As mentioned above, the formation of bainite can only occur when the thermodynamic criteria for both nucleation and growth are satisfied. At the onset of transformation the criterion for nucleation is that

$$\Delta G_m < G_N \tag{3.21}$$

and the growth criterion is that the driving force for transformation without a composition change exceeds the stored energy of bainite:

$$\Delta G^{\gamma \to \alpha} < -400 \text{ J mol}^{-1} \tag{3.22}$$

This last expression defines the T'_0 curve, but both the nucleation and growth criteria must be satisfied during transformation. As the austenite carbon concentration increases during transformation, the magnitude of both ΔG_m and $\Delta G^{\gamma \to \alpha}$ will decrease. Eventually the reaction will cease when one criterion is not satisfied. The value of θ , the maximum allowable volume fraction at the reaction temperature, is taken as the ferrite volume fraction when reaction ceases, regardless of whether termination is by a failure of the nucleation or the growth criterion.

Let x_{N_0} represents the austenite carbon concentration when the nucleation criterion fails and $x_{T'_0}$ when the growth criterion fails. If the driving force is assumed to vary linearly with the extent of reaction, between its initial value ΔG_m^{0} and its final value when the reaction terminates, then

$$\Delta G_m = \Delta G_m^{\ 0} - \xi (\Delta G_m^{\ 0} - G_N) \tag{3.23}$$

This equation is inaccurate when $x_{N_0} > x_{T'_0}$, but this is not a significant problem since the model also includes a growth criterion in which reaction ceases when the fraction θ is achieved. The form of the equation has the additional advantage in that the linear function of ξ preserves the ability to integrate the final differential equation representing the overall transformation kinetics analytically.

A comparison of the x_{N_0} and $x_{T'_0}$ curves for the steel 300 M is shown in Figure 3.4, demonstrating that they are in fact quite close to each other, and that both curves lie well below the Ae'_3 curve which is the $\alpha + \gamma/\gamma$ paraequilibrium phase boundary.

3.3.3 Autocatalysis

Steels with a high carbon concentration eject more carbon from the newly transformed ferrite than lower carbon steels. The build up of carbon at the ferrite-austenite interfaces



Figure 3.4 Comparison of the x_{N_0} and $x_{T'_0}$ curves for the steel 300 M. The Ae3' curve represents the paraequilibrium $\alpha + \gamma/\gamma$ phase boundary.

will cause a temporary local decrease in the driving force for diffusionless transformation. The process of further nucleation on the previously formed plates (*i.e.* autocatalysis) will be inhibited by this carbon build up. This suggests that the autocatalysis factor used in the kinetics model should in some way be dependent on the overall carbon concentration of the alloy. For simplicity the following assumption is used

$$\beta = \lambda_1 \left(1 - \lambda_2 \overline{x} \right) \tag{3.24}$$

where \overline{x} represents the mean carbon concentration of the alloy, and β is the autocatalysis factor (equation 3.4) with λ_1 and λ_2 being empirical constants. In this way, the effect of autocatalysis is less for high carbon steels than for those with lower carbon content. The additional nucleation sites introduced as transformation proceeds is then specified by equation 3.4.

3.3.4 The Effect of Austenite Grain Size

The original model neglected to include a specific austenite grain size effect. The nucleation rate of a grain boundary-nucleated transformation can be assumed to be proportional to the surface area of austenite grain boundaries per unit volume S_V . The reason for this is that the number of suitable sites for nucleation is expected to be directly proportional to the surface area of γ/γ grain boundaries within the sample.

Stereological theory relates S_V to the mean linear intercept \overline{L} of a series of random lines with the austenite grain boundaries, by the expression (DeHoff & Rhines, 1968)

$$S_V = 2/\overline{L}.\tag{3.25}$$

In the new expression for the nucleation rate of bainite the term K_1 will be a function of the austenite grain size, as expressed by the mean linear intercept

$$K_1 = (\overline{L}K_1')^{-1} \tag{3.26}$$

where K'_1 is an empirical constant.

3.3.5 Final Expression

The modifications discussed above can be incorporated into a new model as follows. The volume fraction increment between times t and t + dt is

$$\theta d\xi = (1 - \xi) u I dt \tag{3.27}$$

where u is the sub-unit volume and I is the nucleation rate of bainite per unit volume. The expression for the nucleation rate of bainite can be substituted into this equation giving a differential equation for the overall transformation rate of bainite

$$\frac{d\xi}{dt} = \frac{uK_1}{\theta} (1-\xi)(1+\beta\theta\xi) \exp\left\{-\frac{K_2}{RT}\left(1+\frac{\Delta G_m^{\ 0}}{r}\right) + \Gamma_2\xi\right\}$$
(3.28)

where Γ_2 is given by

$$\Gamma_2 = \frac{K_2(\Delta G_m^{\ 0} - G_N)}{rRT} \tag{3.29}$$

The solution of this equation has the same form as in the previous theory *i.e.*

$$t = \frac{\theta \left(-A \ln \{1 - \xi\} + \frac{B}{\beta \theta} \ln \{1 + \beta \theta \xi\} + \frac{C}{\Gamma_2} \left(1 - e^{-\Gamma_2 \xi}\right) \right)}{u K_1 \exp \left\{ -\frac{K_2}{RT} - \frac{K_2 \Delta G_m^{0}}{rRT} \right\}}$$
(3.30)

The constants were determined by optimising the theory using the same data as used by Bhadeshia (1982b). In this way a direct comparison between the two theories can be obtained.

3.3.6 Interpretation of the Experimental Data

The compositions of the steels used for the original analysis are given in Table 3.2.

	С	Si	Mn	Ni	Mo	Cr	V
Fe-Mn-Si-C	0.22	2.03	3.00	0.00	0.00	0.00	0.00
Fe-Ni-Si-C	0.39	2.05	0.00	4.08	0.00	0.00	0.00
300 M	0.44	1.74	0.67	1.85	0.83	0.39	0.09

Table 3.2 Compositions (wt.%) of the steels used for determination of the reaction kinetics of bainite.



Figure 3.5 A plot of the isothermal transformation kinetics data obtained by Bhadeshia for the Fe-Mn-Si-C steel, as used for the optimisation of the original kinetics model (Bhadeshia, 1982b).

The experimental data were obtained by dilatometry, over a variety of temperatures within the bainitic transformation range. These length change data were analysed using the procedure outlined by Bhadeshia (1982b), given in Appendix 1. For each individual reaction the data were then normalised with respect to the maximum extent of reaction to produce datasets of normalised volume fraction ξ versus time t, for the purpose of evaluating the unknown constants.

Figures 3.5–3.7 show plots of the experimental isothermal transformation kinetics data obtained by Bhadeshia for the Fe–Mn–Si–C, Fe–Ni–Si–C and 300 M steels respectively. Of the three steels, 300 M shows the most consistent behaviour, with the other steels occasionally showing odd results for transformation under similar conditions. It is obvious that a mathematical model cannot reproduce results that are intrinsically inconsistent in this way.

In the case of the Fe-Mn-Si-C steel two transformation runs, at 409°C and 357°C gave particularly dubious results. The optimisation of the model was carried out after discarding those points, though the calculations were also carried out including the rogue points, in order to investigate their effect on the overall agreement.

3.3.7 Grain Size Measurement

The original model contains no account of the effect of the austenite grain size on trans-



Figure 3.6 A plot of the isothermal transformation kinetics data obtained by Bhadeshia for the Fe–Ni–Si–C steel, as used for the optimisation of the original kinetics model (Bhadeshia, 1982b).

formation kinetics. In order to incorporate the effect, the austenite grain sizes produced in the three steels after austenitisation for 5 min at 1000°C were measured. The samples were quenched after austenitisation and then tempered for 1 hr at 600°C, in order to enhance the delineation of the prior austenite grains. The specimens were mounted, ground, polished and etched in 2% Nital for optical metallography. Grain size was represented by the mean linear intercept of a series of random lines with the grain boundaries, on scanning electron micrographs of the microstructure. Table 3.3 gives the results of the mean linear intercept measurements. The number of measurements was in each case 100, giving a statistical error of about $\pm 10\%$

Steel	Mean Linear Intercept/ μ m				
Fe-Mn-Si-C	47 ± 5				
Fe-Ni-Si-C	52 ± 6				
300 M	86 ± 9				

Table 3.3 Mean Linear Intercept values for the austenite grain size of the high silicon steels, after austenitisation at 1000° C for 5 minutes.



Figure 3.7 A plot of the isothermal transformation kinetics data obtained by Bhadeshia for the steel 300 M, as used for the optimisation of the original kinetics model (Bhadeshia, 1982b).

3.3.8 Numerical Analysis

To utilise the new model, it is necessary to determine four constants: K'_1/u , K_2 , λ_1 and λ_2 . This is one less than in the original model, because of the new condition which ensures that the nucleation rate is constant at W_S . Their values were adjusted to give the best agreement between the theory and the experimental data, subject to the condition that the sum

$$\sum \left(\ln \left\{ t_p \right\} - \ln \left\{ t_m \right\} \right) \tag{3.31}$$

is minimised, where t_p denotes the predicted reaction time and t_m denotes the experimental reaction time. The logarithm of these terms is taken because otherwise the error at larger time dominates the sum. A computer algorithm (given in Appendix 2) was developed to search downhill for a minimum to the above sum. The program was terminated when no significant improvements could be achieved.

In order to investigate the origin of any scatter in the agreement between predicted and experimental reaction times the model was optimised with respect to the data from each individual steel as well as with respect to the combined data from all the steels. In the case of the computer runs involving just one steel, there is no variation in the carbon content, and therefore the constant λ_2 was set to zero.
3.4 Results

Figure 3.8 shows plots of predicted versus experimental reaction times using the original and the new theory. The results for individual steels are shown in Figures 3.9–3.11. These plots correspond to steels Fe–Mn–Si–C, Fe–Ni–Si–C and 300 M respectively. The calculations are all summarised in Table 3.4.

Dataset	$K_1'/u \ (\mathrm{m^2 \ s})$	$K_2(\mathrm{J}\ \mathrm{mol}^{-1})$	λ_1	λ_2
Combined data	33.90×10^6	2.065×10^4	139.00	25.46
Fe-Mn-Si-C	38.76×10^6	1.925	4.756	0.00
Fe-Ni-Si-C	20.28×10^6	2.907×10^4	90.822	0.00
300 M	12.308×10^6	3.767×10^4	141.66	0.00

Table 3.4 Best fit values of constants after optimisation of the new theoryusing different datasets.

The effect of including the rogue data from the Fe–Mn–Si–C steel is shown in Figure 3.12a, which should be compared against Figure 3.8b. There is a deterioration in the overall agreement. Figure 3.12b (to be compared with Fig. 3.9) shows how the rogue data reduce the agreement with theory, for the Fe–Mn–Si–C on its own. Table 3.5 gives the best fit values for the constants when the rogue data are included in the numerical analysis.

Dataset	$K_1'/u \ (\mathrm{m}^2 \ \mathrm{s})$	$K_2(\mathrm{J} \mathrm{\ mol}^{-1})$	λ_1	λ_2
Combined data	19.92×10^{6}	2.624×10^4	259.20	39.69
Fe-Mn-Si-C	19.18×10^{6}	$6.395 imes 10^3$	9.696	0.00

Table 3.5 Best fit values of constants when the numerical analysis includes the rogue data in the Fe–Mn–Si–C experiments.

3.4.1 Application of The New Theory

The improvements due to the new analysis can be highlighted by comparison with the original model. Figure 3.13 shows the predicted transformation behaviour of Steels 1 and 2 at 470 °C. As can be seen, the high-manganese steel is now predicted as transforming slower than Steel 2, which has a smaller manganese concentration. Trends due to alloying element concentrations are therefore correctly predicted, unlike the data illustrated in Figure 3.2. Figure 3.14 shows the effect of temperature on the transformation behaviour of 300 M. The reaction kinetics are shown as increasing with decreasing temperature, as was observed experimentally, again





Figure 3.8 Comparison of predicted and experimentally determined reaction times for the bainite reaction in high silicon steels. a) Original theory. b) New theory.



Figure 3.9 The degree of agreement between predicted and experimental reaction times for the steel Fe–Mn–Si–C after optimising the theory with respect to the data from this steel alone.

correcting the erroneous prediction by the original model. A computer program for calculating the isothermal reaction profiles of steels at temperatures below B_S is presented in Appendix 3. It can be seen by comparing the plots in Figure 3.8, that the new theory gives a significant improvement in the agreement between the measured and predicted reaction times. Data from each of the individual steels are also shown to be broadly consistent with the theory, though the constants derived by individual optimisation differ from those consistent with the best overall fit. The reasons for this effect are not clear and it is particularly worrying that the best fit constants for the Fe–Mn–Si–C steel are so different from the other alloys. Nevertheless, the form of the transformation curves is clearly well represented by the model.

The results can be summarised in a TTT diagram. Figure 3.15 shows the predicted TTT diagrams for Steel 1 and Steel 2, illustrating the fact that the manganese-rich steel transforms more slowly and that the reaction kinetics increase with decreasing temperature. A notable feature is that the predicted curves do not show the usual C-curve shape seen in some experimental diagrams. An examination of published TTT curve atlases reveals that this is not unexpected in high-hardenability alloys, although it is also worth pointing out that the present analysis takes no account of carbide precipitation, so that detailed comparisons are not in general possible.



Figure 3.10 The degree of agreement between predicted and experimental reaction times for the steel Fe–Ni–Si–C after optimising the theory with respect to the data from this steel alone.

Most of the TTT curve data are on steels not used in the bainitic condition, whereas modern bainitic steels are designed to avoid carbide precipitation.

The absence of a C-shape could be real (as indicated by the experimental data for 300 M steel) or may be attributed to other factors which have been neglected. It has been consistently reported that the apparent thickness of bainitic sub-units varies as a function of the transformation temperature (Bhadeshia, 1982b; Pickering, 1958; Ohmori, Ohtani & Kunitake, 1971). It is not possible, however, to model this size variation without relaxing the condition that the steels have the same nucleation rate at W_S , though we have verified that such size variation would indeed result in a C-shaped TTT curve.

3.5 Conclusions

An earlier model for the overall transformation kinetics of bainite in steels where carbide precipitation can be suppressed, has been corrected and refined to be consistent with the known mechanisms of bainite nucleation and growth. The precision of the new model in estimating the rate of reaction is found to be better, and the model has a greater degree of internal consistency and one less disposable constant. The overall agreement between theory and experiment can be made good by optimising the values of four parameters, two of which describe autocatalysis, and



Figure 3.11 The degree of agreement between predicted and experimental reaction times for the steel 300 M after optimising the theory with respect to the data from this steel alone.

the other two describing the nucleation phenomena. It is suggested that these parameters can be used for all steels (where carbide formation is suppressed). Although much better agreement can be obtained when the parameter values are fixed by comparing the experimental data for just one steel against theory, the procedure is not justified because the parameters appear to vary haphazardly with alloy chemistry.





Figure 3.12 The effect on the degree of agreement with the new model of including the rogue data from Fe-Mn-Si-C. Plot (a) shows the deterioration in overall agreement. Plot (b) shows the best fit for the Fe-Mn-Si-C steels considered alone.



Figure 3.13 Comparison of the predicted reaction rates of Steel 1 and Steel 2, (compositions are given in Table 3.1) at 470°C using the new bainite kinetics model. The higher manganese content of Steel 2 results in a slower transformation, as expected, correcting the error in the original model.



Figure 3.14 The predicted effect of temperature on the transformation of 300 M. The kinetics are predicted as increasing as temperature decreases, as observed experimentally, correcting the error in the original model.



Figure 3.15 Comparison of the predicted TTT curves for Steel 1 and Steel 2 using the new model. The curves illustrate the prediction that highly alloyed steels react more slowly than lightly alloyed steels and that the reaction rate increases with undercooling below B_S .

CHAPTER 4

Bainite Transformation Kinetics & the Non-Uniform Distribution of Carbon

4.1 Introduction

Bainite in steels tends to grow in the form of clusters of small, parallel plates known as 'sub-units', each of a limited size and with all sub-units within a particular sheaf having the same crystallographic orientation (Bhadeshia & Christian, 1990; Christian & Edmonds, 1984). The individual plates within a sheaf, although interconnected in three dimensions, can be separated along most of their surfaces by thin films of untransformed austenite especially in steels where carbide precipitation reactions are suppressed (it is these steels that are considered here) (Bhadeshia & Christian, 1990; Christian & Edmonds, 1984). This is in contrast to the large blocks of austenite which may remain untransformed as bainite sheaves growing in different directions impinge on one another. Figure 4.1 shows untransformed austenite regions of both types.

The maximum extent of the bainite reaction in steels is limited by the carbon which diffuses from the supersaturated bainitic ferrite plates into the untransformed austenite immediately after transformation. Such steels are of considerable technological importance, both from the point of view of ultra high strength alloys and welding alloys. The partitioned carbon enriches the austenite to such a degree as reaction proceeds, that the driving force for transformation eventually reaches zero. The reaction then stops, even though substantial amounts of untransformed austenite remain in the microstructure.

Bainite transformation kinetics have in the past been calculated assuming that the carbon is homogeneously distributed in the residual austenite, but there is now considerable evidence to suggest that this is not the case. The films of austenite between the ferrite plates are to a large extent, isolated by the surrounding ferrite. They can achieve carbon concentration levels which are far in excess of the levels expected assuming a homogeneous distribution. Such 'trapping' of excess carbon in the isolated films would intuitively be expected to lead to a larger maximum volume fraction of ferrite, since the carbon concentration in the larger blocks of untransformed austenite will be correspondingly smaller at any stage of reaction. There is some experimental evidence for this. Continuous cooling experiments in which the cooling rate is so slow that there is a greater opportunity for partitioned carbon to homogenise, show that a larger degree of transformation is obtained when the carbon is inhomogeneously distributed (Khan & Bhadeshia, 1990).



Figure 4.1 Schematic diagrams indicating the location of untransformed austenite in bainitic microstructure. a) Blocky regions of austenite between sheaves. b) Thin films of carbon enriched austenite between bainitic sub-units.

The purpose of this work is to examine theoretically, the extent to which the trapping phenomenon influences both the kinetics and the maximum extent of transformation that can be achieved at any temperature, using the theory developed in Chapter 3. The modifications and improvements made to the original kinetic theory are incorporated and extended in this chapter.

4.2 Accounting for the Trapping of Carbon

The treatment of bainite kinetics as presented in Chapter 3 supposes that the carbon that is rejected from the transformed bainitic ferrite is homogeneously distributed in the untransformed austenite. In reality, some of the austenite is in the form of isolated films between the plates of ferrite. The carbon that diffuses into these films becomes trapped there and should therefore change the way in which the reaction proceeds. A modification is presented below which takes account of the expected inhomogeneous distribution of carbon.

Some simplifying assumptions are necessary. It is assumed that one film of austenite is trapped for each sub-unit of bainite that grows. It is well established that the films trapped within sheaves are carbon-enriched to concentrations which are in general much larger than that expected from the T'_0 curve (explained in Chapter 3). Therefore, it is assumed that the films are saturated with carbon. The composition of the austenite films is then given by the value of the Ae'_3 curve at the reaction temperature. (This is the composition of austenite at the paraequilibrium $\alpha + \gamma/\gamma$ phase boundary). The paraequilibrium phase boundary is chosen because no substitutional alloying element partitioning occurs during bainite formation. Considering a unit volume of austenite, a volume u is assigned to each bainitic sub-unit, and a volume v_t to each film of trapped austenite.

By a mass balance argument the carbon content x_B of the untransformed blocky austenite after n plates of ferrite have formed in a unit volume of sample, (*i.e.* when the volume fraction of ferrite is nu) is:

$$x_B = \frac{\overline{x} - nu[x_{\alpha} + (v_t/u)x_{Ae'_3}]}{1 - nu[1 + (v_t/u)]}$$
(4.1)

where \overline{x} is the mean carbon content of the the alloy; x_{α} is the carbon concentration of the ferrite; $x_{Ae'_{\alpha}}$ is the carbon content of the austenite saturated with carbon.

The reaction of austenite to ferrite will cease when the composition of the austenite has reached the T'_0 value (Christian & Edmonds, 1984; Khan & Bhadeshia, 1990). This is the carbon concentration at which ferrite with a strain energy of 400 J mol⁻¹ has the same free energy of as austenite of the same composition, which therefore makes it the limiting austenite composition that can support transformation to bainite.

By rearrangement of the above expression a maximum allowable volume θ' can be calculated. This corresponds to the condition where the carbon concentration of the blocky austenite has reached the T'_0 value.

$$\theta' = \frac{\overline{x} - x_{T'_0}}{[x_{\alpha} + (v_t/u)x_{Ae'_3}] - [1 - (v_t/u)x_{T'_0}]}$$
(4.2)

It is possible however, for the austenite to become enriched in carbon to such an extent that the *nucleation* of ferrite by a displacive mechanism is impossible, before the carbon content of the austenite reaches $x_{T'_0}$ (which is the determined by driving force for bainite growth). Under these conditions, if x_{N_0} represents the carbon content at which nucleation ceases then the maximum allowable extent of transformation is

$$\theta' = \frac{\overline{x} - x_{N_0}}{[x_{\alpha} + (v_t/u)x_{Ae'_3}] - [1 - (v_t/u)x_{N_0}]}$$
(4.3)

Regardless of whether the termination of reaction occurs because the available driving force is insufficient for nucleation or for growth it is convenient to express the mole fraction of ferrite in terms of a normalised volume fraction:

$$\xi' = v/\theta' \tag{4.4}$$

where, as demonstrated above, the actual volume fraction of ferrite v = nu.

4.3 Computational Details

The assumption that all films are of identical volume is of course an approximation. It is difficult to estimate the relative thicknesses of the plates and films in a meaningful way, since bainitic plates often touch along some of their surfaces. A series of hypothetical values are therefore used to represent the film thickness so that the sensitivity of the predicted transformation rate to the trapping effect can be investigated.

Calculations were performed for three hypothetical steels of different carbon and substitutional solute content (Table 4.1). Since it is anticipated that carbon trapping will affect both the driving force and the allowable extent of reaction it is of interest to perform calculations comparing reactions for two cases:

(a) alloys with different carbon levels but with the same driving force;

(b) two alloys with the same carbon content, but different driving force.

Alloy No.	С	Si	Mn
A1	0.1	2.0	2.0
A2	0.2	2.0	1.87
A3	0.1	2.0	1.5

Table 4.1 Compositions (wt.%) of the steels chosen for investigating the predicted effect of trapping of carbon in retained austenite films.

Alloy A2 was chosen to have the same driving force as alloy A1 at 500°C so that special consideration could be given to the relative reaction rates at this temperature. Alloy A3 has the same carbon content in weight percent as alloy A1, though the mole fraction of carbon will be slightly different for the two alloys. The important thermodynamic quantities for the three alloys at 500°C are shown in Table 4.2. For all three alloys at this temperature it was found that $x_{T'_0}$ was less than x_{N_0} . Termination of reaction will therefore be due to a failure of the thermodynamic criterion for growth in all three cases. The maximum extent of transformation is therefore calculated using $x_{T'_0}$.

It is also noteworthy that the maximum allowable fraction of ferrite for alloys A1 and A2 will be different at 500°C since the carbon content is different. Carbon can also affect the reaction kinetics by altering the auto-catalysis factor. It is therefore anticipated that the trapping phenomenon will affect the lower carbon alloy to a greater extent than for the higher carbon alloys, since a greater fraction of the total carbon will be trapped in the thin film austenite.

Alloy No.	$\Delta G_m^{\ 0}/\mathrm{J} \mathrm{\ mol}^{-1}$	β	\overline{x} (at. frac.)	$x_{T'_0}$ (at. frac.)	$x_{Ae'_3}$ (at. frac.)
A1	-880	148.79	4.541×10^{-3}	1.396×10^{-3}	5.678×10^{-3}
A2	-880	125.12	9.050×10^{-3}	1.447×10^{-3}	5.194×10^{-3}
A3	-996	148.78	4.542×10^{-3}	1.673×10^{-3}	6.582×10^{-3}

Table 4.2 Comparison of parameters affecting the predicted kinetics of the bainite transformation at 500° C. The values are independent of the effect of trapping of carbon, and account for some of the differences in transformation rate shown in Figure 4.2

4.4 Results

Figure 4.2 shows the calculated effect of the presence of trapped high-carbon austenite films on the predicted reaction profiles of alloys A1, A2 and A3 at 500°C. Table 4.2 gives the values of the important parameters from the bainite reaction kinetics theory for these three steels at the reaction temperature, so that a comparison can be made. Four different film thicknesses are considered, with values such that

$$v_t/u = 0.005, 0.01, 0.015, 0.02$$

The reason for choosing these particular values is that it was hoped to investigate the effect of trapping of carbon while avoiding the condition in which *all* the carbon partitioned from the bainitic ferrite was trapped in the austenite films.

4.5 Discussion

Examination of the results in Figure 4.2 shows that for steels with equal driving forces at the same transformation temperature the carbon content of the alloy determines the magnitude of the effect of trapping. The extent of reaction and the transformation kinetics are affected to a greater degree in the lowest carbon alloy, with the effect of carbon on the auto-catalysis factor greatly affecting the overall transformation rate. For steels with similar carbon content but



Figure 4.2 The calculated effect of the presence of trapped austenite films on the bainite kinetics of the three hypothetical steels whose compositions are listed in Table 4.1

different driving force the effect of trapping on the extent of transformation is very similar. In these cases the different reaction kinetics are mainly a result of the difference in driving force, since the effect of auto-catalysis is the same in both alloys. Though the fraction of carbon trapped in the two steels is dependent on the respective Ae'_3 compositions, it appears that the magnitude of the effect is similar in both cases.

Intuition suggests that the presence of trapped films will have the largest effect on the extent of transformation and the kinetics of transformation for the low carbon alloy in the series being investigated. This is because, with the film composition set equal to the Ae'_{3} composition a larger fraction of the total carbon content of the alloy will be trapped.

The trend in the calculations that the reaction is faster for the case of the larger film thickness *i.e.* the larger the amount of carbon that is trapped, the faster the reaction proceeds. The limiting case is when the film thickness is related to the phase compositions by the expression

$$\frac{v_t}{u} = \frac{\overline{x} - x_\alpha}{x_{Ae'_3}}$$

since this represents the condition when all carbon partitioned by the ferrite ends up in the thin-film austenite. Since, under this condition there will be no enrichment of bulk untransformed austenite, reaction can proceed until all the bulk austenite is consumed. The resulting microstructure would then consist solely of bainitic ferrite and thin film carbon–enriched austenite.

Considering the effect of trapping on the maximum extent of the bainite reaction for the series of alloys shows that the magnitude of the increase in maximum volume fraction produced by the inhomogeneous distribution of carbon does not vary significantly with substitutional alloying element concentration. This is to be expected, because the effect of trapping is mainly dependent on the proportion of the total carbon that is trapped. The substitutional alloying element concentration can affect the T'_0 and N_0 compositions, but terms such as these are mainly dependent on driving force, so that their effect should be hidden when a comparison is made at constant driving force.

The higher carbon steels show less sensitivity to the presence of trapped carbon. A smaller fraction of the total carbon is trapped between the sub–units in these cases. The maximum possible extent of transformation is also smaller. Consequently, the number of sheaves and the the corresponding number of austenite films available for trapping is reduced.

4.6 Conlusions

The non-uniform distribution of carbon due to the trapping of carbon in isolated austenite films leads to an acceleration of transformation. It further leads to an increase in the limiting fraction of bainitic ferrite that can be obtained at any temperature. Steels that have low carbon content are shown to be more sensitive to trapping effect because a greater fraction of the total carbon can then be accommodated in the films.

Carbide precipitation from austenite is most likely to occur from the film austenite which is richer in carbon. The present model could in fact be used to estimate the effect of such carbide precipitation of transformation kinetics. The carbides in effect remove carbon from the austenite, in a manner similar to the way in which the films of austenite isolate excess carbon from the reacting bulky regions of austenite.

CHAPTER 5

The Microstructure of High Strength Steel Welds

5.1 Background

A programme of research has been carried out (Svensson & Bhadeshia, 1988; Bhadeshia & Svensson, 1989) with the aim of producing a tough, high strength steel multi-pass weld, to be fabricated by the submerged arc, or the core continuous wire process. A novel approach to solving this problem was devised by the authors. In order to achieve good toughness it was desired to eliminate the detrimental phases, allotriomorphic ferrite and Widmanstätten ferrite from the microstructure, since these phases are relatively brittle. Other significant proposals for controlling the weld microstructure were also made, as discussed below.

It has been demonstrated the the toughness of the primary weld deposit shows greater scatter if the microstructure consists of more than one phase. The presence of Widmanstätten ferrite and allotriomorphic ferrite together with acicular ferrite therefore increases the scatter in toughness as well as decreasing the mean toughness. Tweed & Knott (1987) also suggest that toughness is improved by mechanical homogeneity in the weld, which implies that microstructural homogeneity is beneficial. Since many desired welds are multi-pass deposits it was necessary to ensure that the properties of the reheated regions of the weld are essentially similar to those of the primary weld metal.

In order to achieve this goal of uniform mechanical properties in multi pass welds it was proposed by Bhadeshia & Svensson that the composition of the weld deposit should be chosen so that the Ae'_3 temperature is reduced. This increases the tendency of the reheated regions to reaustenitise, and to transform to a microstructure similar to that of the primary regions on subsequent cooling. In order to ensure that regions of the weld that do not reaustenitise are not adversely affected by reheating, good temper resistance of the microstructure was considered essential.

In order to produce the high weld metal strength it was necessary to aim for a microstructure of acicular ferrite and martensite. A microstructure of acicular ferrite alone (*i.e.* with a very small fraction of martensitic microphases) cannot produce weld metal strength greater than \approx 700MPa. Since martensite can have a detrimental effect on the toughness of a weld deposit it was necessary to lower the carbon content of the alloys in order to avoid the formation of relatively brittle high-carbon twinned martensite. The partitioning of carbon in to the untransformed austenite as a result of the formation of ferrite at higher temperatures means that the martensite that forms will have a higher carbon content than the bulk alloy. Carbides forming within tempered martensite can help nucleate cleavage cracks and voids. Low carbon martensite has the added advantage of a better temper resistance *i.e.* a reduced tendency to form carbides on tempering, since the martensitic ferrite then forms with a lower carbon supersaturation. The presence of silicon in the microstructure also helps inhibit cementite formation. Any loss of strength from the tempering process will be decreased if the temper resistance of the weld is increased, thereby improving the mechanical homogeneity of the weld.

The approach to the problem of developing a tough high-strength uniform weld was therefore to use intelligent additions of alloying elements to achieve the simultaneous goals of lowering the Ae'_{3} temperature, producing a microstructure of acicular ferrite and martensite in the primary and reaustenitised regions, lowering the carbon content of martensite, and increasing the temper resistance of the microstructure as a whole.

Using the weld microstructure model a series of compositions were predicted as giving primary weld deposits with volume fractions of allotriomorphic ferrite and Widmanstätten ferrite of zero, or close to zero. The microstructure of this type of weld is therefore predicted as consisting of a mixture of acicular ferrite and 'microphases' only. The term 'microphases' is misleading in this context, since the fraction of acicular ferrite in the series is approximately 0.5 The relatively high hardenability of the steels selected suggests that any austenite remaining untransformed after the acicular ferrite reaction will decompose to martensite. This was confirmed by Bhadeshia & Svensson (1988) using transmission electron microscopy (TEM), in their preliminary examination of an experimental weld from this series. Hardness traverses across the fusion boundary in the experimental weld revealed that strength was maintained well as the microstructure changed from the as-deposited to the reaustenitised or tempered regions.

5.2 The Problem

The effect of increasing the substitutional alloy content on the microstructure of low alloy steel deposits is shown schematically in Figure 5.1. The weld microstructure model developed by Bhadeshia, Svensson and Gretoft (1986-1991) determines the volume fraction of acicular ferrite by difference *i.e.* since, apart from a small amount of martensite, it is the last phase to form, its fraction can be determined by subtracting the fractions of the other phases from unity.

$$V_{\alpha_a} = 1 - V_\alpha - V_{\alpha_W} - V_m$$

where the subscripts α_a , α_W and m denote acicular ferrite, Widmanstätten ferrite and microphases including martensite. This method of determining the acicular ferrite content assumes that the fraction of martensite and other microphases can be estimated by thermodynamic approximations.

If the concentration of austenite stabilising elements is sufficiently large, transformation temperatures are depressed to such an extent that reconstructive transformations are too slug-



Figure 5.1 A schematic representation of the effect of increasing the austenite stabilising substitutional solute content on the the microstructure of low alloy steel welds.

gish to occur within the time scale of the cooling of the weld. Allotriomorphic ferrite will not then be present. By further alloying, the temperature at which displacive nucleation becomes possible is also lowered beneath that at which ferrite can grow by a displacive mechanism (Bhadeshia 1981a). This means that the formation of Widmanstätten ferrite does not occur, since by the time the nucleation of this phase becomes possible, it will possible to form bainite and acicular ferrite. It is expected, though, that further alloying will affect the relative volume fractions of acicular ferrite and martensite in the microstructure.

Since martensite and acicular ferrite have different properties, the strength and toughness of the weld is expected to be dependent on the relative volume fractions of these phases. Modelling of the microstructure is therefore of great potential importance in assessing and predicting the mechanical properties of the weld. An aim of the present work was to characterise the microstructure of welds of systematically varying chemistry in order to establish an experimental database of use in testing a microstructure prediction model.

5.3 Experimental Techniques

5.3.1 Materials

A series of ten experimental welds were provided by ESAB AB (Sweden), with a systematic

variation in the alloying element concentrations. The compositions of the welds are given in Table 5.1 with the dominant variation highlighted. Alloy 90 is the weld originally investigated by Bhadeshia & Svensson and its composition is included for comparison. Alloy 112 essentially reproduces that chemistry. Also of considerable interest is the trace element content of the welding alloys. The concentrations of oxygen, nitrogen, aluminium, titanium and sulphur are listed in Table 5.2. Trace element variations are expected to lead to differences in the inclusion chemistries of the welds, the chemistry being a possible source of microstructural variation via the nucleation of acicular ferrite. The welding parameters used in fabrication are listed in Table 5.3.

Alloy No.	С	Si	Mn	Ni	Mo	\mathbf{Cr}	V
90	0.07	0.3	1.22	2.02	0.39	0.49	0.008
112	0.062	0.26	1.30	2.18	0.38	0.44	0.00
113	0.059	0.47	1.48	2.00	0.37	0.63	0.00
114	0.079	0.53	1.64	2.32	0.42	0.69	0.00
115	0.059	0.48	2.02	2.20	0.41	0.65	0.025
116	0.053	0.46	1.08	2.20	0.41	0.65	0.022
117	0.054	0.46	1.53	3.01	0.41	0.66	0.022
118	0.052	0.44	1.51	1.52	0.41	0.66	0.022
119	0.067	0.47	1.53	2.13	0.57	0.64	0.022
120	0.052	0.44	1.58	2.18	0.24	0.64	0.020
121	0.052	0.42	1.51	2.23	0.41	0.90	0.022
122	0.054	0.43	1.56	2.30	0.42	0.36	0.021

Table 5.1 Compositions of the alloys in the high strength weld series. All compositions are in wt%. Highlighted numbers indicate the major changes in chemistry relative to alloy 112.

5.4 Characterisation of the Weld Microstructure

5.4.1 Comparison of Microscopic Techniques

Optical Microscopy

Optical microscopy proved ineffective in characterising the microstructure of the welds in the experimental series. The scale of the microstructure is fine and the appearance of the two phases, acicular ferrite and martensite, both being plate-like, is too similar to be easily differentiated. Figure 5.2 shows an example of an optical micrograph of alloy 113 (centre bead,

Alloy No.	0	Ν	Al	Ti	S
90	322	76	200	40	70
112	363	81	220	40	60
113	304	55	220	60	50
114	267	47	220	70	60
115	358	56	150	20	50
116	356	45	150	20	50
117	398	52	150	20	50
118	411	49	140	20	50
119	415	52	180	20	50
120	481	50	150	20	50
121	468	52	150	20	50
122	397	46	150	20	50

Table 5.2 The trace element composition (ppm by weight) of the welding alloy series.

Alloy No.	Current/A	Voltage/V	Speed/m hour ⁻¹	Interpass Temperature/°C
90	580	29	33	200
112	580	29	33	200
113	500	29	30	200-250
114	500	29	30	200-250
115	500	29	30	200-250
116	500	29	30	200-250
117	500	29	30	200-250
118	500	29	30	200-250
119	500	29	30	200-250
120	500	29	30	200-250
121	500	29	30	200-250
122	500	29	30	200-250

Table 5.3 Welding variable values for the alloy series. All weld were made by the submerged arc process.



Figure 5.2 A typical optical micrograph of the structure of alloy 113, illustrating the difficulty in resolving the ultra-fine microstructure.

top layer). As can be seen, there is insufficient resolution to allow any quantitative estimation of the volume fractions of the phases present.

Scanning Electron Microscopy (SEM)

Conventional SEM images are difficult to interpret, but the use of the image inversion feature on the CAMSCAN S2 microscope enables a more easily recognisable microstructure to be seen. The reason for this is that by etching in nital, the acicular ferrite is attacked preferentially compared with the martensite, leaving the martensitic regions slightly elevated on the etched surface. Image inversion gives the appearance of raised acicular ferrite plates surrounded by martensite. SEM is the ideal instrument for recording microstructures at sufficiently high resolution for quantitative evaluation of the microstructural components while still enabling sufficiently large areas of the weld to be sampled so that local variations in the microstructure are taken into account. Great care was taken therefore to obtain the best possible SEM images of the welds.

Transmission Electron Microscopy (TEM)

The high magnification and resolution that TEM provides enables unambiguous identification of the microstructural components in the welds. A typical carbon replical TEM micrograph



Figure 5.3 A typical carbon replica electron micrograph of the primary region of a steel weld deposit (after G.S. Barrite, 1982).

of an acicular ferrite and martensite structure is shown in Figure 5.3, where the different microstructural components are clearly distinguished. However, for the purpose of characterising and quantifying the microstructure of a weld, a large area needs to be sampled so that effects such as variations in acicular ferrite plate size, and the effect of chemical segregation can be examined. Investigation of weld microstructure on this scale makes TEM unsuitable. This can be illustrated by considering that Bhadeshia & Svensson approximated the volume fraction of acicular ferrite in alloy 90 to be around 0.4 using TEM, whereas SEM reveals a much higher fraction of this phase in the microstructure as a whole. Examination of SEM micrographs in this chapter demonstrates how, in many alloys, the occurrence of martensite islands is highly localised. Martensite islands of this kind occur in addition to the martensite which forms between acicular ferrite plates, and is probably a result of chemical segregation. The use of TEM could miss this important microstructural feature, simply by failing to sample a large enough area, even if many specimens were examined. Carbon replica work on TEM provides essentially similar results to SEM since it is the surface topography of etched specimens that is examined.

5.4.2 Microhardness Testing and Hardness Traverses

The microstructure of the high strength weld can also be characterised by the microhard-

ness of the primary weld deposit. Steels with a larger volume fraction of martensite are expected to have higher hardness values, though alloying element content and other factors can also affect hardness. A model which attempts to account for all the factors affecting the hardness of the primary weld deposit is presented in the following chapter. Trends in hardness can therefore be linked to trends in the volume fraction of the phases in the welds. Of great importance is the need for mechanically homogeneous welds, in which the absence of microstructural inhomogeneity imparts reproducibly good toughness which can be exploited successfully by reducing scatter. Microhardness traverses were performed across the fusion line of the primary weld bead into the reaustenitised and reheated regions of selected alloys in order to investigate any trends in properties that could result from refinement of austenite grain size, differences in cooling behaviour after reaustenitisation, and possible tempering effects. The alloys chosen for this investigation were alloys 119, 120, 121, 122 *i.e.* those with systematic variations in the concentration of molybdenum and chromium, elements which can cause secondary hardening.

5.4.3 Microstructural Homogeneity

A series of SEM micrographs was taken for two particular welds from the series, alloy 113 and alloy 114. The micrographs covered an area which included the columnar grained austenite region of the primary weld metal, into the equiaxed austenite grains of the reaustenitised region of the neighbouring bead. The reaustenitised regions of the weld were distinguished by the isotropic, equiaxed appearance of the austenite grains, with regions of columnar grains close to the reaustenitised material being interpreted as tempered.

The object of this exercise was to investigate any change in microstructure arising from the different austenite grain morphology; the reaustenitised weld metal can transform to bainite if the austenite grain size is sufficiently small *i.e.* the number density of grain boundary nucleation of sites increases relative to the inclusion site density to cause grain boundary nucleation of bainite to dominate over the intragranular nucleation of acicular ferrite (Yang & Bhadeshia, 1987). The size to which an austenite grain will grow depends on the maximum temperature experienced, as well as on the kinetics of reaustenitisation. Other factors such as the pinning of the austenite grains by particles in the weld metal may also be important. The effect of the heat input on previously deposited metal decreases with distance from the heat source, and therefore a gradation of austenite grain size within the reheated region was expected. Regions of bainite in the reheated microstructure were therefore searched for. Since bainite is known to exhibit lower fracture resistance than acicular ferrite the presence of such regions could be detrimental to the weld properties as a whole.

The austenite grain structure of the weld was investigated by etching polished specimens in saturated picric acid in methanol which contained an addition of wetting agent, namely sodium

di-octyl sulfosuccinate. The microstructural observations were carried out after repolishing and etching in 2% Nital. The use of this etching technique is after Frost *et al.* (1987). The etchant composition is given in Table 5.3.

The choice of alloys for this investigation was made in order to gain a comparison between the behaviour of a steel which gave a high volume fraction of acicular ferrite in the as-welded condition (alloy 113) with another which showed a smaller acicular ferrite fraction (alloy 114).

Composition	99ml Saturated Picric Acid in methanol
	0.1% di octyl sulfo succinate
Method	Etch in an ultrasonic bath for 2 minutes

Table 5.3 Details of the composition and treatment conditions of the picric acid based grain boundary etchant (after Frost *et al.* 1987)

5.4.4 Quantification of the Microstructure

Interpretation of the microstructure is far from trivial. It is impossible to rule out certain errors arising from the subjective nature of the process of interpretation. The 'three dimensional' appearance of SEM images produces variations in 'grey level' resulting from shadowing effects, making the use of image-analysis difficult. A process of tracing the acicular ferrite in the microstructure before image-analysis involves the same interpretation process as does point counting, and was found to be less readily applicable since tracing could not follow very fine features in the microstructure.

The volume fraction of acicular ferrite in each weld was determined by superimposing a rectangular grid of 378 points on the SEM micrograph, which gives a statistical error of around $\pm 5\%$ in measurement. Clearly plate-like regions appearing raised above the sample surface were interpreted as acicular ferrite and the inter-plate regions interpreted as martensite. The volume fraction of acicular ferrite was calculated using the expression

$$v_{\alpha_a} = \frac{N_{\alpha_a} + N_{\rm ind}/2}{N_{\alpha'} + N_{\alpha_a} + N_{\rm ind}}$$

where N_{α_a} and $N_{\alpha'}$ represents the number of points lying on regions of acicular ferrite and martensite respectively, with N_{ind} representing the number of indeterminate points. The points classed as indeterminate corresponded to regions of the microstructure that were difficult to interpret *e.g.* if a point fell on the boundary between an acicular ferrite plate and an inter-plate region, or when it was impossible to identify the microstructural component beneath the point. Half of such points were assumed to correspond to acicular ferrite.

5.5 Results

5.5.1 Microstructural Observations

The Effect of Variation of the Major Alloying Elements

Figures 5.4, 5.5 and 5.6 show the effect on the weld deposit microstructures of changes in the concentration of the major alloying elements. Figures 5.4 (a) and (b) show the essentially similar microstructures of alloys 112 and 113. Figure 5.5 (a) shows a high magnification image of alloy 112, with the microstructure of high carbon alloy 114 given in Figure 5.5 (b). The effect of manganese variation is shown by Figure 5.6 (a) and (b) which show the microstructures of alloys 115 and 116 respectively.

The Microstructural Effect of Chemical Segregation

Figure 5.7 (a) shows an example of the pronounced banding observed in the microstructure of alloy 114. Figure 5.7 (b) shows a solute depleted region of alloy 115 with a high fraction of accoular ferrite, markedly different from the microstructure shown in Figure 5.6 (a).

The Effect of Variation of Other Substitutional Solute Elements

Figure 5.8 (a) and (b) show the changes in weld microstructure as the nickel concentration is changed. Alloys 117 and 118 are respectively the high and low nickel variants of the series. Nickel has an intrinsic beneficial effect on the toughness of steel and this constitutes a major reason for its popularity in weld deposits. In body centered cubic iron, screw dislocations lying along < 111 > directions are dissociated in three dimensions on the three $\{11\overline{2}\}$ planes sharing the common < 111 > axis. The degree of dissociation is extremely small but is large enough to cause an increase in the flow stress with a consequent decrease in toughness. Nickel increases the stacking fault energy, thereby reducing the extent of dislocation dissociation, and hence makes plastic flow easier. The corresponding lowering of the ductile/brittle transition temperature is the major reason for the presence of nickel in high strength steels weld deposits.

Nickel does, of course, have other benefits e.g. it reduces the driving force for the transformation from austenite to ferrite (*i.e.* it is an austenite stabiliser) although its influence is not as pronounced as that of manganese.

The effect of increasing the molybdenum content of the weld deposit is shown in Figures 5.9 (a) and (b) which display the microstructures of alloy 119 and alloy 120, the high and low-molybdenum members of the alloy series respectively. Chromium variation effects are shown in Figure 5.10 (a) and (b), which show the respective microstructures of alloy 121 and 122.

5.5.2 Comparison of As-deposited and Reheated Microstructures

Figure 5.11 shows the change in the austenite grain morphology across the fusion boundary of the centre bead on the top layer. Figure 5.12 (a) and Figure 5.12 (b) show the microstructure

of the reaustenitised regions of alloy113 and alloy 114 respectively. The equiaxed shapes of the reaustenitised grains are clearly evident.

5.5.3 Microhardness Testing

Figure 5.13 and 5.14 show the results of microhardness traverses across the fusion boundary between the centre bead of the top layer and a neighbouring underlying bead for alloys 113 and 114 respectively. Marked on the plots are the regions P1 and P2 corresponding to the columnar regions of the as-deposited microstructure. A layer of reaustenitised material separates these columnar grained regions.

Figures 5.15 and 5.16 show hardness traverse results across the fusion boundary into the reheated regions of alloy 119 and alloy 120 respectively. Figures 5.17 and 5.18 show hardness traverses across the fusion boundary of alloys 121 and 122. The microstructures of alloy 119 and alloy 121 in reaustenitised and tempered regions of the heat affect weld metal are shown in Figures 5.19 and 5.20 respectively.

5.5.4 Volume Fraction Measurements

The volume fraction of acicular ferrite in each alloy, as determined by point counting on high magnification micrographs is shown in Table 5.5. The data from Table 5.4 is presented graphically in Figure 5.21

5.6 Discussion

5.6.1 Microstructure of the Primary Weld Metal

Alloy 112 (Standard Alloy)

Figure 5.4 (a) illustrates all the essential features of the structure of a prototype high strength steel weld. It consists of fine acicular ferrite and martensite mixture with the volume fraction of acicular ferrite being very large. The columnar austenite grains are clearly visible and are free from phases such as allotriomorphic ferrite or Widmanstätten ferrite. The acicular ferrite plates show some size variation, although this could be a stereological effect. The uniformity of the microstructure is remarkable as is the number density of acicular ferrite plates. None of the plates have developed to any appreciable length because the nucleation sites are so closely spaced that physical impingement with other plates occurs soon after the plates become large enough to be visible. The low magnification image shows evidence of a small amount of chemical segregation, although this does not seem to have a profound effect on the microstructure, presumably because the kinetics of transformation are in any case quite rapid. In welds it is the substitutional alloying element segregation which leads to the major microstructural effects – ferrite forms in regions depleted of austenite-stabilising elements and

Alloy	Acicular Ferrite Fraction ± 0.5
A112	0.75
A113	0.78
A114	0.43
A115	0.53
A116	0.76
A117	0.53
A118	0.78
A119	0.54
A120	0.75
A121	0.58
A122	0.66

Table 5.5 Volume fraction measurements of acicular ferrite in the primary weld metal region of a variety of weld deposits. The measurements were in each case made for the centre bead in the top layer. The balance of the microstructure is martensite.

the carbon partitioned from the ferrite produces bands of carbon-enriched martensite. Thus the low carbon content of the alloys used here minimises any consequences of substitutional solute segregation.

Alloy 113 (Low Carbon)

This alloy was intended to be a lower carbon version of alloy 112, but it was difficult in practice to achieve a large reduction because of the raw material used in electrode manufacture. Hence its chemical composition is only slightly different from alloy 112. This fact is reflected in a very similar microstructure, as shown in Figure 5.4 (b). As expected, the effects of chemical segregation are less obvious again in alloy 113, presumably because of the somewhat smaller carbon content of the alloy. The volume fraction of acicular ferrite is found to be large.

Alloy 114 (High Carbon)

The effect of increasing the carbon content of the weld deposit is shown by comparing the high magnification image of alloy 112 in Figure 5.5 (a) with the high magnification image of alloy 114 in Figure 5.5 (b). Alloy 114 represents a significantly higher carbon variant (0.079 wt%), and its microstructure reflects this. The high magnification image reveals significantly larger quantities of martensite and a correspondingly lower fraction of acicular ferrite. The acicular

ferrite plate shapes are much more prominent since their development has been influenced to a lesser degree by impingement with other plates nucleated on adjacent inclusions. Indeed there is a clear tendency for acicular ferrite *sheaves* to develop probably because the nucleation rate on inclusions has been reduced by the higher carbon content. A further consequence of the increased carbon content is that bands containing large amount of martensite can be observed frequently (*e.g.* Fig. 5.7 (a)). This results from substitutional solute segregation whose very prominent effect on the microstructure is exaggerated by the partitioning of large amounts of carbon in to the solute-depleted regions, as can clearly be seen in the low magnification image of alloy 114 shown in Figure 5.7 (a).

It should be noted that although the carbon concentration of 0.079 wt% is not much greater than the 0.062 wt% of alloy 112, the development of the microstructure is very sensitive to carbon variations at low carbon concentrations. This is because the mean carbon concentration approaches the solubility of carbon in ferrite.

Manganese Variation

Figure 5.6 (a) shows the microstructure of the high manganese alloy 115. An increase in the manganese concentration (c.f. alloys 112, 115) seems to have a similar effect to the increase in carbon, giving a large amount of martensite in the microstructure. The tendency for forming sheaves of acicular ferrite seems to be somewhat lower than for the high carbon variant. Thus it would appear advantageous from the point of view of mechanical properties to achieve high strength via manganese alloying rather than by an increase in the carbon concentration.

A reduction in the manganese concentration in alloy 116, shown in Figure 5.6 (b) leads to the expected microstructure containing almost exclusively acicular ferrite, whose morphology is similar to that of alloy 112. Allotriomorphic ferrite and Widmanstätten ferrite are found to be absent despite the lower manganese concentration. It is apparent from comparing alloys 112, 114, 115 and 116 that the higher alloy content alloy 114 and 115 have finer acicular ferrite plate sizes, despite the fact that the nucleation rate of these alloys is lower than for alloys 112 and 116. It is likely therefore that the fine size of the acicular ferrite plates is a result of the temperature of formation rather than impingement effects. For bainite, apparent plate thickness has been consistently reported to increase as the transformation temperature increases (Bhadeshia, 1982b; Pickering, 1958; Ohmori, Ohtani & Kunitake, 1971).

The Effect of Chemical Segregation on Microstructure

Solute segregation between the solidifying weld metal and the liquid is assumed to be the cause of the clear banding in the microstructure of the high carbon alloy 114 (Fig. 5.7 (a)). This banding is made more pronounced by the large difference in the amount of martensite

in the microstructure. It appears that the microstructure of the alloy is very sensitive to the substitutional alloy content in this high carbon variant of the series.

In the high manganese alloy 115, a high magnification micrograph from a solute depleted region of alloy 115, is shown in Figure 5.7 (b). Comparing this image with that of the bulk of material within the primary weld metal it can be seen that the effects of long range chemical segregation have a profound effect on the microstructure. A decrease in the substitutional solute content increases the driving force for ferrite formation, thus increasing the transformation rate. It appears that the resultant microstructure is sensitive to the solute content, but to a lesser extent than is seen in alloy 114, since the carbon level of the alloy is smaller.

Nickel Variation

A large nickel concentration (Fig. 5.8 (a)) increases the martensite fraction in the microstructure, whereas a reduction (alloy 118, Fig. 5.8(b)) below the concentration in alloy 112 does not have much of an effect. The lack of change on lowering the nickel concentration is because the difference made to the transformation kinetics between alloys 112 and 118 is not large. Nickel also has a large partition coefficient with liquid iron and consequently has a greater tendency to segregate (Gretoft *et al.* 1986). Thus bands of martensite are apparent in the low magnification image of alloy 117.

Molybdenum and Chromium Variations

The effects of both molybdenum and chromium on the primary microstructure are as expected; an increase in the concentration of each element relative to alloy 112 leads to an increase in the martensite volume fraction, and vice versa. This effect is shown in Figures 5.9 and 5.10 which display the microstructures of the high molybdenum, low molybdenum, high chromium and low chromium variants respectively. Apart from the effect on the fraction of acicular ferrite, as will be discussed later, the major effect manifests itself in the multi-pass deposits where the secondary hardening tendency of Mo and Cr assumes significance.

5.6.2 Comparison of As-Deposited and Reheated Microstructure

A significant difference in the γ grain morphology across the fusion boundary can be seen in Figure 5.11 which shows the austenite grain structure of alloy 113. The grain structure is revealed by using saturated picric acid in methanol with a small addition of sodium di-octyl sulfosuccinate as an etchant. As can be seen from Figure 5.12 (a) the microstructure of Alloy 113 is very similar in the columnar grained region and in the equiaxed region of the multi-pass weld. Figure 5.12 (b) show that this is also the case for alloy 114. The finer grain size of the equiaxed region has resulted in a slightly greater proportion of bainite, but the effect of cooling reaustenitised material at a different the cooling rate in the reheated regions has not increased the tendency to form other grain-boundary nucleated phases such as allotriomorphic ferrite and Widmanstätten ferrite.

5.6.3 Hardness Traverses

Figures 5.13 and 5.14 show that the variation of hardness across the fusion boundary of alloy 113 and alloy 114 is small, in comparison with the variations in hardness that arise from statistical errors and the local variation in the microstructure of the welds. In combination with the micrographs of the structure in the columnar and reheated regions, the hardness traverses emphasise the mechanical and microstructural homogeneity of the welds. The results indicate the achievement of the goals of the designers in producing a weldment composition that would maximise the tendency to reaustenitise the reheated regions, while ensuring that these regions transformed to a structure similar to that of the as-deposited regions after the passing of the arc.

Comparison of the hardness traverses across fusion boundaries in alloy 119, 120, 121 and 122, given in Figures 5.15, 5.16, 5.17 and 5.18 respectively, show that there is little change in hardness between the as-deposited, reaustenitised and tempered regions. This observation is particularly significant for the welds that have a high concentration of elements which promote secondary hardening. The variation of the hardness is small compared to the general scatter in microhardness measurements. It is likely that the small carbon content of the alloys makes the precipitation of carbides unlikely within the time scale of the reheating process. The significance of the absence of secondary hardening effects is that the mechanical homogeneity of the weld is not affected adversely by the choice of the alloy chemistry.

The microstructure changes associated with the hardness traverses in alloy 119 and alloy 121 are illustrated in Figure 5.19 and Figure 5.20 respectively. In each case micrograph (a) represents the microstructure of the central reaustenitised region, with micrograph (b) illustrating the microstructure of near the final indent of the hardness traverse, in the columnar region of a tempered bead.

5.6.4 Volume Fraction Measurements

The volume fraction measurements of acicular ferrite listed in Table 5.5 show the expected general trend that the more highly alloyed steels should display a higher volume fraction of martensite than the lightly alloyed variants of the series. These data are displayed graphically in Figure 5.21.

5.7 Conclusions

From the microstructural observations it can be concluded that the the most potent factor in determining the extent of transformation to acicular ferrite in weld deposits that do not form any allotriomorphic ferrite or Widmanstätten ferrite is the carbon concentration of the alloy. The presence of austenite stabilising substitutional solutes (e.g. Mn and Ni) also inhibits the formation of acicular ferrite. The marked effect of solute segregation in the high carbon alloy 114 indicated how much more sensitive the microstructure of the weld deposit is to the substitutional alloy content when the level of carbon is raised.

In the manganese or nickel-rich weld deposits, regions can be found in the weld that have significantly higher acicular ferrite fractions than the bulk of the deposit. The scale of these variations is larger than the banding observed in alloy 114, but is presumably a consequence of substitutional alloy partitioning. It is noteworthy that the large difference in microstructure between alloy 113 and alloy 115 is essentially achieved by a change in the manganese content of 0.5 wt%. So sensitive is the microstructure to alloy composition that substitutional element partitioning during solidification need not be dramatic in order to achieve significant changes in microstructure.

In the alloys where the amount of acicular ferrite is small, it is common to see a clustering of ferrite plates in sheaf structures rather than the more classic structures desired in welds. The lower nucleation rate of the more highly alloyed steels makes nucleation on inclusions less rapid and therefore autocatalytic effects become more important *i.e.* acicular ferrite plates have the opportunity to nucleate on previously formed plates before hard impingement with neighbouring sites makes this impossible. It is also significant that there is a clear size difference in the plates of the highly alloyed steels compared to those in the more lightly alloyed variants of the series. This is a result of the different temperatures at which the bulk of transformation occurs during the cooling of the weld; the reaction start temperature depends on the alloy chemistry.

The microstructural homogeneity of the multi-pass welds studied is found to be remarkable. Austenite grain boundaries appear free of allotriomorphic ferrite and Widmanstätten ferrite except for isolated regions in some leaner alloys. The effect of chemical segregation, however, does cause second order variations in the microstructure. In the high carbon alloy the variation of the microstructure due to segregation occurs within individual columnar grains. In the high manganese alloy solute depleted regions can be found where whole columnar grains appear to show a much higher acicular ferrite fraction than in the bulk alloy.

Hardness traverses across the fusion boundaries of alloys in the series reveal no observable trends in the properties of the deposit resulting from effects such as tempering and the difference in austenite grain size. In steels in which the concentration of secondary hardening elements is high, there is no evidence of a marked increase in the hardness of the tempered regions. This fact is interpreted as indicating that the low carbon content of the alloys prevents significant precipitation of the alloy carbides that cause secondary hardening.



Figure 5.4 a) The microstructure of alloy 112 (standard alloy) which shows the essential characteristics of high strength steel weld deposits. A finer grained region of possible solute enrichment due to segregation is arrowed. b) The microstructure of alloy 113, essentially similar to that of alloy 112.



Figure 5.5 a) A high magnification image of the microstructure of alloy 112. b) The microstructure of alloy 114, the high carbon variant of the alloy series. Both micrographs are of the centre bead on the top layer of the weld.



Figure 5.6 a) The microstructure of the high manganese weld deposit, alloy 115. b) The microstructure of alloy 116, low manganese variant of the alloy series. Both micrographs are of the centre bead on the top layer of the weld.



Figure 5.7 a) A micrograph of as-deposited alloy 114 showing the pronounced banding in the microstructure resulting from solute segregation. b) A micrograph of a solute depleted region in as-deposited alloy 115, showing a large fraction of acicular ferrite.


Figure 5.8 a) The as-deposited microstructure of alloy 117, the high nickel member of the alloy series, with region of high martensite content arrowed. b) The as-deposited microstructure of the low nickel variant, alloy 118.



Figure 5.9 a) The as-deposited microstructure of alloy 119, the high molybdenum member of the alloy series. b) The as-deposited microstructure of lowmolybdenum alloy 120.



Figure 5.10 a) The as-deposited microstructure of high-chromium alloy 121. b) The as-deposited microstructure of the low chromium alloy 122.



Figure 5.11 The outline of prior austenite grains across the boundary between the as-deposited and the reheated regions in alloy 113.



Figure 5.12 a) A micrograph of the reaustenitised metal of alloy 113 in the heat affected region of a previously deposited bead. b) A micrograph of the reaustenitised material in the a heat affected region of alloy 114.



Figure 5.13 Hardness traverse across the fusion boundary in alloy 113.



Figure 5.14 Hardness traverse across the fusion boundary in alloy 114.



Figure 5.15 Hardness traverse across the fusion boundary in alloy 119, the high molybdenum variant of the alloy series.



Figure 5.16 Hardness traverse across the fusion boundary in alloy 120, the low molybdenum variant of the alloy series.



Figure 5.17 Hardness traverse across the fusion boundary in alloy 121, the high Chromium variant of the alloy series.



Figure 5.18 Hardness traverse across the fusion boundary in alloy 122, the low Chromium variant of the alloy series.



Figure 5.19 a) The microstructure of high-temperature reaustenitised weld metal in alloy 119. b) Microstructure of the columnar region of tempered weld metal in alloy 119.



Figure 5.20 a) The microstructure of high-temperature reaustenitised weld metal in alloy 121. b) Microstructure of the columnar region of tempered weld metal in alloy 121.



Figure 5.21 A graphical presentation of the measured acicular ferrite fractions in the as-deposited regions of the experimental weld series.

CHAPTER 6

Modelling the Microstructure and Properties of High Strength Steel Welds

6.1 Introduction

Following characterisation of the microstructure of a series of experimental high strength steel welds provided by ESAB, an attempt is made here to predict the microstructure from a knowledge of the chemical composition and thermal history of each weld alone. An attempt is also made to predict some mechanical properties from knowledge of the weld microstructure.

Existing models for the strength of welds (*e.g.* Sugden & Bhadeshia, 1988) are inadequate when applied to the type of weld considered here since the models group acicular ferrite and microphases together as one microstructural component. In microstructures consisting of substantial fractions of acicular ferrite and martensite it is necessary to account for the effect of these two phases separately. We begin with the methodology for estimating the microstructure, which is then related to the mechanical properties.

6.2 Previous Work

The weld microstructure model developed by Bhadeshia and co-workers is based on the following procedure:

- (a) From knowledge of the chemical composition of the weld, the composition of the solutedepleted regions of the weld is estimated (Gretoft *et al*, 1986).
- (b) Thermodynamic methods are used to estimate transformation temperatures such as M_S , B_S and Ae'_3 (Bhadeshia 1981a, 1981b, 1981c; Shiflet *et al*, 1978).
- (c) The theory for TTT-curve prediction (Bhadeshia, 1982a) is used to estimate the isothermal transformation diagram for the solute depleted regions of the weld. The start temperature for the allotriomorphic ferrite reaction is estimated using the Scheil approximation.
- (d) The start temperature for Widmanstätten ferrite is obtained by calculating the cross-over point of the predicted upper and lower C-curves (Bhadeshia *et al*, 1985).
- (e) Between the upper and lower limits set as its transformation temperature range allotriomorphic ferrite is assumed to grow by a paraequilibrium mechanism consistent with the diffusion of carbon in the austenite ahead of the interface (Bhadeshia *et al*, 1985).
- (f) Between its calculated start time and an empirically-set limiting time for impingement with intragranularly nucleated phases, Widmanstätten ferrite is assumed to grow with kinetics estimated by the Trivedi theory for plate lengthening (Trivedi & Pound, 1969).
- (g) The calculated volume fractions of the determined phases are subtracted from unity, giving the acicular ferrite fraction determined by difference (Bhadeshia *et al*, 1985). Note that the calculated acicular ferrite content therefore includes any microphases.

6.3 Application of the Bainite Kinetics Model to the Acicular Ferrite Reaction

6.3.1 The Connection Between Bainite and Acicular Ferrite

It has been argued by Yang and Bhadeshia (1987) that acicular ferrite and bainite are in fact identical in transformation mechanism, the morphological difference between them arising during nucleation. Bainite does so on austenite grain boundaries, whereas acicular ferrite nucleates on the non-metallic inclusions present inside the austenite grains. The plates of acicular ferrite therefore radiate in many different directions from what are, in effect, point nucleation sites. The following features are common to acicular ferrite and bainite:

• They both display the incomplete reaction phenomenon *i.e.* reaction ceases before the equilibrium or paraequilibrium volume fraction of ferrite has formed. (Bhadeshia & Edmonds, 1979, 1980).

• Both the phases show surface displacements consistent with a macroscopic invariant plane strain (IPS) shape change. (Strangwood & Bhadeshia, 1987).

• Both phases can form 'upper' and 'lower' forms (Sugden & Bhadeshia, 1989) distinguishable by the presence or absence of carbide precipitation in the ferrite. Upper bainite and acicular ferrite have carbides precipitated only in the austenite between the ferrite plates. Lower bainite and lower acicular ferrite have carbides situated within the ferrite phase. There is a competition between the decarburisation of the supersaturated ferrite by partitioning of carbon into the austenite, and carbide precipitation from supersaturated ferrite. In upper bainite and upper acicular ferrite precipitation of carbides within the ferrite cannot occur rapidly enough to prevent complete decarburisation by diffusion into the surrounding austenite. (Takahashi & Bhadeshia, 1990)

• In reheated weld metals, forming acicular ferrite in the as-welded condition, bainite can be induced to form instead if the austenite grain size is reduced in order to increase the number density of grain boundary nucleation sites relative to those within the austenite grains (Yang & Bhadeshia, 1987). Alternatively, if grain boundary nucleation is inhibited by decorating the austenite grain surfaces with thin layers of allotriomorphic ferrite, then the acicular ferrite microstructure is recovered (Babu & Bhadeshia, 1990).

In view of the similarities between the acicular ferrite and bainite reactions it seems appropriate to apply the bainite kinetics theory to acicular ferrite, and to model development under conditions of continuous cooling.

6.3.2 Assumptions

The attempt to apply the improved theory of bainite transformation kinetics (Chapter 3) to acicular ferrite requires the following assumptions:

The thermodynamics of the two processes are considered to be the same (Yang & Bhadeshia 1987). This means that acicular ferrite has the same driving force and limiting volume fraction as bainite at any temperature below the bainite-start temperature.

The autocatalysis process and the value of the autocatalysis constant are assumed to be the same for acicular ferrite and bainite, despite the fact that acicular ferrite does not usually form sheaves. It is clear though, from the microstructures of some experimental welds that sheaf formation in acicular ferrite is indeed possible. It seems likely that impingement with the products of other nucleation events within the austenite grains is the factor that inhibits sheaf development for acicular ferrite.

6.3.3 Time-Temperature Profile of a Cooling Weld

The cooling behaviour of an arc weld can be well represented by the expression (Svensson, Gretoft & Bhadeshia, 1986)

$$\frac{dT}{dt} = \frac{\epsilon_1 \left(T - T_{\rm int}\right)^{1 - \epsilon_2}}{Q\eta} \tag{6.1}$$

where the interpass temperature is represented by T_{int} . The electrical energy input Q and the arc transfer efficiency η are process-dependent variables. The terms ϵ_1 and ϵ_2 are material-dependent empirical constants. The expression can be integrated to give

$$t = Q\eta \left(\frac{(T_0 - T_{\rm int})^{1 - \epsilon_2}}{(1 - \epsilon_2)} - \frac{(T - T_{\rm int})^{1 - \epsilon_2}}{(1 - \epsilon_2)} \right)$$
(6.2)

where T_0 represents the initial temperature *i.e.* at t = 0, for convenience set at 900 °C. The submerged arc and manual metal arc welding processes are distinguished by the heat input and arc transfer efficiency terms. For the submerged arc welds investigated in the present work the values of ϵ_1 , ϵ_2 and η were (Svensson, 1988)

 $\epsilon_1 = 4359$ $\epsilon_2 = 1.51$ $\eta = 0.95$

6.3.4 Application of the Bainite Kinetics Model to Continuous Cooling

As discussed in Chapter 3, the bainite kinetics expression can be expressed by the differential equation

$$\theta \frac{d\xi}{dt} = K_1 (1 - \xi) (1 + \beta \theta \xi) I \{T, \xi\}$$
(6.3)

where the temperature dependence of the nucleation rate, as well as its dependence on the extent of reaction are represented in general form for brevity. The time dependence of temperature can be expressed by the cooling rate equation (eqn. 6.2), but quantities such as driving force and phase boundary compositions are calculated by iterative methods, and hence it is impossible to express the time dependence of the bainite volume fraction as an explicit function of temperature.

For continuous cooling heat treatments it is therefore necessary to use a numerical summation to evaluate the volume fraction of bainitic ferrite formed as a weld cools. The calculation procedure is outlined below

(1) If the maximum volume fraction of ferrite that can form at temperature T is θ , let the time t, taken to form an actual volume fraction v at temperature T be represented in a general form as

$$t = t \{v, T\} \tag{6.4}$$

The normalised volume fraction ξ formed after isothermal transformation at temperature T for time t is therefore

$$\xi = \xi \left\{ t, T \right\} \tag{6.5}$$

where

$$v = \xi \theta \tag{6.6}$$

- (2) The time-temperature profile of the weld is separated into one degree steps, as shown schematically in Figure 6.1. The continuous cooling curve is therefore approximated as a series of short isothermal steps. At temperature T_i the duration of the isothermal hold is Δt_i, and the maximum allowable fraction of bainite or acicular ferrite is θ_i.
- (3) At step i = 1 the volume fraction of ferrite formed after the end of the first isothermal step Δt_1 is calculated. *i.e.*

$$v_1 = \theta_1 \xi \{ \Delta t_1, T_1 \}$$
 (6.7)

(4) At the second isothermal temperature, the effective time t_{e_2} necessary for formation of the fraction v_1 at this temperature is calculated *i.e.*

$$t_{e_2} = t \{ v_1, T_2 \} \tag{6.8}$$

(5) The ferrite is then allowed to grow for the duration of the second isothermal hold Δt_2 .

$$v_2 = \theta_2 \xi \left\{ t_{e_2} + \Delta t_2, T_2 \right\}$$
(6.9)



Figure 6.1 The approximation of a continuous time-temperature profile as a series of short isothermal steps. The isothermal step step length Δt_i is defined.

(6) At subsequent temperatures T_i , the effective time t_{e_i} necessary to form the existing volume fraction is calculated. The calculated volume fraction for a general temperature is then v_i where

$$v_i = \theta_i \xi \left\{ t_{e_i} + \Delta t_i, T_i \right\} \tag{6.10}$$

with

$$t_{e_i} = t\left\{v_{i-1}, T_i\right\} \tag{6.11}$$

Reaction-Start and Reaction-Finish Temperatures

Acicular ferrite, being similar to bainite, can only form when the appropriate thermodynamic criteria for nucleation and growth are satisfied. The criterion for growth is that (Bhadeshia, 1981a)

$$\Delta G^{\gamma \to \alpha} = -400 \text{ J mol}^{-1} \tag{6.12}$$

where $\Delta G^{\gamma \to \alpha}$ is the free energy change for transformation from austenite to ferrite of the same composition. The condition which must be satisfied for nucleation is that

$$\Delta G_m^{\ 0} < G_N \tag{6.13}$$

at the reaction temperature (Bhadeshia, 1982a). ΔG_m^0 represents the maximum free energy change for formation of a small amount of ferrite from austenite, and G_N is the universal function representing the value of ΔG_m at which nucleation by a displacive mechanism becomes possible.

Once the temperature of the cooling weld has fallen below M_S there is sufficient driving force to form martensite. Since martensite is favoured kinetically over bainite and acicular ferrite, it is assumed that the acicular ferrite formation stops once martensite formation has begun.

Attempts to account for the depression of the M_S temperature of the untransformed by carbon enrichment were not successful. Using the empirical expression for the estimation of the M_S (Bhadeshia, 1981b, 1981c) resulted in the prediction that the untransformed austenite would never transform to martensite since, as reaction to acicular ferrite proceeded the predicted M_S temperature decreased faster than the actual temperature.

6.3.5 Nucleation Site Density

Since it is known that the nucleation of bainite and acicular ferrite occurs on different sites, it is unlikely that the previously determined value of the nucleation site density dependent constant for bainite kinetics, K_1 , can be applicable to acicular ferrite. This constant was therefore varied in order to produce the best agreement between the predicted and experimental observed acicular ferrite fractions for the alloy series as a whole.

An attempt was made to weight the nucleation site density parameter in proportion to the calculated inclusions content (Kluken & Grong, 1989) of the weld (Figure 6.2). This involved multiplying the K_1 for each alloy, by a factor proportional to the inclusion content. The data in Figure 6.2 is presented according to the amount of oxygen present (ppm by weight) in each type of inclusion.

The following different methods for weighting were tried in order to investigate the potency of particular oxides

- (1) MnO content;
- (2) Al_2O_3 content;
- (3) combined Al_2O_3 and MnO content;
- (4) no weighting.

The computer program used for the calculation of the acicular ferrite volume fraction formed during continuous cooling is presented in Appendix 4.

6.4 Properties of High Strength Steel Welds

When phases are all present present in substantial fraction it is a convenient assumption to



Figure 6.2 Calculated inclusion content of the alloys in the high strength weld metal series. The inclusion content is represented by the oxygen (ppm by weight) present as each oxide type.

suppose that the overall yield strength of a weld metal can be expressed as a 'rule of mixtures', in which each of the phases contributes according to its strength and volume fraction.

This assumption has been successfully applied by Sugden (1988) to estimate the strength of weld deposits containing allotriomorphic ferrite, Widmanstätten ferrite and acicular ferrite. Central to that work was the evaluation of the microstructural contribution to the strength of the phases *i.e.* different forms of ferrite have different strengths due to their different morphologies. This microstructural contribution to the strength of the deposit was determined for each of the phases. Acicular ferrite and the microphases were grouped together, and hence the microstructural strengthening term deduced for acicular ferrite actually applies to the combination of phases which this grouping can represent. Since, in many cases, the microphases were probably martensitic, it is possible that the microstructural contribution to the strength of acicular ferrite was overestimated. In any case, for present purposes, where microstructures consist of substantial amounts of both acicular ferrite and martensite, it is necessary to consider these phases separately.

Let σ_{α_a} , $\sigma_{\alpha'}$ and σ_y represent the yield stresses of the acicular ferrite, martensite and the resultant two-phase microstructure. Applying the 'rule of mixtures' approximation to the strength of the weld deposit, the overall yield strength can be expressed as

$$\sigma_y = V_{\alpha_a} \sigma_{\alpha_a} + \left(1 - V_{\alpha_a}\right) \sigma_{\alpha'} \tag{6.14}$$

6.4.1 Modelling the Hardness of Martensite

The strength of martensite as function of alloy and carbon composition can be estimated using the empirical relationship for the Vickers hardness of martensite determined by Maynier, Jungmann & Dollet (1978) *i.e.*

$$HV = 127 + 949c_{\rm C} + 27c_{\rm Si} + 11c_{\rm Mn} + 8c_{\rm Ni} + 16c_{\rm Cr} + 21\log(\rm V_R)$$
(6.15)

where c_i refers to the concentration of the *i*th element (wt %), and V_R represents the cooling rate experienced by the steel (°Cs⁻¹). Unfortunately, this expression was determined for steels of rather higher carbon concentration than those under present investigation and so it was decided to establish our own empirical model for the hardness of martensite. Since carbon is known to affect the yield strength of steel in proportion to the square root of its concentration (Speich & Warlimont, 1968), and other elements in small concentrations are assumed to have a linear effect on strength, the form of the empirical expression for martensite hardness is

$$H_{\alpha'} = k_c c_c^{1/2} + \sum_i k_i c_i + k_0 \tag{6.16}$$

where k_i represents the coefficient of the strength contribution of *i*th element, of concentration $c_i(\text{wt\%})$. The term k_0 is the contribution independent of alloy composition.

The relationship between the Vickers hardness and the 0.2% proof stress of a material can be approximated by (Cahoon *et al*, 1971)

$$\sigma_y = \left(\frac{H}{3}\right) \left(0.1\right)^{m-2} \tag{6.17}$$

where m is the Meyer's hardness coefficient, related to the strain hardening coefficient n by the expression (Tabor, 1951)

$$n = m - 2 \tag{6.18}$$

In the absence of strain hardening data for the weld deposits being considered here, it was decided to use the simplifying assumption

$$\sigma_y = \frac{H}{3} \tag{6.19}$$

despite the fact that Sugden (1987) has argued that this leads to an overestimation of yield strength.



Figure 6.3 The solid solution strengthening effects of various alloying elements of iron (after Leslie, 1972)

The strength of the acicular ferrite in the microstructure was estimated by considering the effect of various substitutional and interstitial alloying elements. Since the solubility of carbon in ferrite if less than $10^{-3}(at\%)$ at room temperature (Hansen, 1958) its solid solution strengthening effect on ferrite is considered negligible. Nitrogen present in the weld is considered to be present in solution. The solid solution strengthening effects of the elements were estimated using data from Leslie (1972). Figure 6.3 displays the solid solution strengthening effects of various substitutional alloying elements on iron (after Leslie 1972). In small concentrations the effect of each element can be combined linearly. The strength of acicular ferrite is then given by (Sugden 1988)

$$\sigma_{\alpha_a} = \sigma_{Fe} + \sum_i x_i \kappa_i + \Delta \sigma_{\rm mic} \tag{6.20}$$

where x_i denotes the atomic fraction of element *i*. The κ_i value for each element is given in Table 6.1. The term $\Delta \sigma_{\rm mic}$ represents the microstructural contribution to the yield strength of acicular ferrite, with σ_{Fe} representing the strength of pure annealed iron.

6.4.2 Experimental Technique

The macro-hardness (VHN) of the as-deposited weld metal was determined for the centre bead of the top layer of each weld. The tests were performed on specimens mounted, polished

Solid	Solid Solution Strengthening Coefficients (MPa/mole)					
κ_{Si}	5215					
κ_{Mn}	3510					
κ_{Ni}	3938					
κ_{Cr}	94					

Table 6.1 Coefficients of solid solution strengthening by substitutional solutes in ferritic iron (Leslie 1972).

and lightly etched in the same manner as used for metallography. The indentation load was 10 kg in all cases. Martensitic specimens were prepared by cutting samples (approximate dimensions $1 \text{cm} \times 1 \text{cm} \times 1 \text{cm}$) from the heart of each weld and quenching in iced water after and austenitisation treatment of 10 minutes at 1000°C. The specimens were sealed in quartz tubes under a partial pressure of pure argon during the austenitisation, with the tube being broken in the quenching bath immediately after removing from the furnace. The macro-hardness values of the martensitic specimens were also determined by taking the mean value from 10 measurements. Table 6.2 gives the composition and hardness values for the as-deposited and martensitic specimens of each alloy.

After determination of the hardness coefficients for martensite it is necessary to express the hardness of martensite in the two phase acicular ferrite and martensite mixture in the as-deposited weld metal. If the volume fraction of acicular ferrite is V_{α_a} then the carbon concentration of the austenite that transforms to martensite is

$$\frac{\overline{x} - x_{\alpha_a} V_{\alpha_a}}{(1 - V_{\alpha_a})} \tag{6.21}$$

making the hardness of the martensite

$$H_{\alpha'} = k_c \left(\frac{\overline{x} - x_{\alpha_a} V_{\alpha_a}}{(1 - V_{\alpha_a})}\right)^{1/2} + \sum_i c_i k_i + k_0$$
(6.22)

The optimum value of the microstructural component of acicular ferrite strength was determined by re-arranging the equation for the total weld deposit hardness so that $\Delta \sigma_{\rm mic}$ could be determined by regression. This was achieved by separating the equation for the overall alloy strength in the following way

$$\sigma_{y} - V_{\alpha_{a}} \left(\sigma_{\mathrm{Fe}} + \sum_{i} x_{i} \kappa_{i} \right) - \left(1 - V_{\alpha_{a}} \right) \sigma_{\alpha'} = V_{\alpha_{a}} \Delta \sigma_{\mathrm{mic}}$$
(6.23)

The left-hand side of the equation was plotted against V_{α_a} so that the gradient of a straight line fitted to the data, forced through the origin, gave the optimum value of $\Delta \sigma_{\rm mic}$.

Alloy No.	С	Si	Mn	Ni	Mo	Cr	H_{tot}	$H_{lpha'}$
90	0.071	0.30	1.22	2.02	0.39	0.49	277 ± 5	398 ± 10
112	0.062	0.26	1.30	2.18	0.38	0.44	264 ± 3	366 ± 5
113	0.059	0.47	1.48	2.00	0.37	0.63	276 ± 3	391 ± 7
114	0.079	0.53	1.64	2.32	0.42	0.69	328 ± 2	400 ± 5
115	0.059	0.48	2.02	2.2	0.41	0.65	297 ± 6	393 ± 6
116	0.053	0.46	1.08	2.2	0.41	0.65	263 ± 2	346 ± 5
117	0.054	0.46	1.53	3.01	0.41	0.66	296 ± 2	393 ± 4
118	0.052	0.44	1.51	1.52	0.41	0.66	268 ± 2	364 ± 5
119	0.067	0.47	1.53	2.13	0.57	0.64	297 ± 4	386 ± 5
120	0.052	0.44	1.58	2.18	0.24	0.64	257 ± 4	369 ± 4
121	0.052	0.42	1.51	2.23	0.41	0.90	292 ± 3	357 ± 6

Table 6.2 Compositions (wt%) and hardness values (VHN) of the as-deposited weld metal and martensitic specimens from the high strength weld metal alloy series.

The volume fraction measurements of acicular ferrite in the microstructures of the high strength weld deposits are listed in Chapter 5. These values, determined by point counting on high magnification SEM images, were used for the optimisation of $\sigma_{\rm mic}$. The computer program for predicting the hardness of the weld microstructures is presented in Appendix 5.

6.5 Microstructure Prediction Results

Figures 6.4, 6.5 and 6.6 show the best fit predictions of acicular ferrite volume fraction when the calculations were weighted according to the MnO content, the Al_2O_3 , the combined Al_2O_3 and MnO content respectively. The best results were, however obtained when no weighting was applied. The acicular ferrite volume fraction prediction for this condition is shown in Figure 6.7, and the agreement with the experimental volume fraction is shown in Figure 6.8 which plots the predicted versus the experimental values.

6.6 Hardness Prediction Results

The hardness coefficients for the martensite hardness expression were determined by a multiple regression algorithm. The best fit constants for this expression are displayed in Table 6.3 together with the standard errors. The optimum value of the microstructural contribution to the strength of acicular ferrite was determined by evaluating the gradient of the best-fit line shown in Figure 6.9. The determination of this value utilised the empirical expression for the



Figure 6.4 The best agreement obtained for predicted *vs.* experimentally measured volume fractions with calculations weighted according to the MnO content of the weld.



Figure 6.5 The best agreement obtained for predicted vs. experimentally measured volume fractions with calculations weighted according to the Al_2O_3 content of the weld.



Figure 6.6 The best agreement obtained for predicted vs. experimentally measured volume fractions with calculations weighted according to the combined Al_2O_3 and MnO content of the weld.



Figure 6.7 Histogram showing the predicted acicular ferrite volume fraction for the alloy series when no weighting was applied to the prediction calculation.



Figure 6.8 A plot of predicted volume fraction versus the experimentally measured volume fraction of acicular ferrite when no weighting was applied to the prediction calculation.

hardness of martensite. The result of this analysis was

$$\Delta \sigma_{\rm mic} = 316 \pm 15 \,\,\mathrm{M}\,\,\mathrm{Pa} \tag{6.24}$$

Using the optimised value of $\Delta \sigma_{\rm mic}$ the hardness of the as-deposited weld microstructures were predicted using the experimentally determined values of the acicular ferrite volume fractions. The resulting agreement between the predicted and experimental hardnesses, shown in Figure 6.10 is good, with a correlation coefficient of 0.94.

6.7 Conclusions

6.7.1 Microstructure Prediction

As can be seen from the best fit prediction of acicular ferrite volume fraction, the trends in the microstructure resulting from the different substitutional solute content of the alloys are reflected correctly in the theoretical predictions. It is apparent however, that the microstructure of the actual weld deposits is more sensitive to the variations in alloy chemistry than the calculation suggest. While it is not clear why this is the case, it is stressed that the constants used in the theory were determined for high-silicon steels, varying only the nucleation site density constant. As will be explained in Chapter 9, it has not proved practical to establish



Figure 6.9 The determination of the microstructural component of the strength of acicular ferrite in the two-phase acicular ferrite and martensite structure of the high strength steel weld deposits. The regression variable is defined as $\sigma_y - V_{\alpha_a} (\sigma_{Fe} + \sum_i x_i \kappa_i) - (1 - V_{\alpha_a}).$



Figure 6.10 The degree of agreement between the predicted and the calculated hardness values of the high strength steels weld deposits.

Hardness coefficient	Regression Value (VHN)	Standard Error (VHN)		
k_C	671	458		
k_{Si}	-73	408*		
k_{Mn}	35	27		
k_{Ni}	13	16		
k_{Mo}	-9	82*		
k_{Cr}	60	418*		
k_0	133	190		

Table 6.3 Results of the regression analysis of the hardness of martensite as a function of alloy composition. Results where the standard error of a hardness coefficient is much greater than the determined value are denoted with *.

the appropriate constants for the acicular ferrite transformation by optimising agreement between the theory and experimental isothermal transformation data. The fact that *trends* in the microstructure are reflected correctly suggests that the application of constants determined for bainite is appropriate for acicular ferrite, but that the optimum values may not have been achieved.

6.7.2 Hardness Prediction

Experimental results and predictions from modelling indicate that increasing the volume fraction of martensite in the weld deposit will increase the overall hardness. Welds that have a high volume fraction of acicular ferrite are correctly predicted as being softer than those which have a high fraction of martensite, despite the fact that a high acicular ferrite fraction results in martensite with a higher carbon concentration. It may be the case however that small regions of high carbon martensite may be detrimental to overall toughness (the avoidance of high carbon martensite was a design aim of this type of weld deposit).

The agreement between predicted and experimental hardness values is good when using the experimentally determined volume fractions of acicular ferrite in the microstructure. It is also necessary to optimise the microstructural contribution to the strength of acicular ferrite in order to produce good results. It is interesting to note that the best fit value of $\Delta \sigma_{\rm mic}$ is smaller than that the previously determined value (Sugden, 1988) where acicular ferrite was grouped together with the microphases in the structure. A possible explanation for this is that, in the original treatment, by grouping the acicular ferrite and microphases together, the strengthening effect of hard microphases (*e.g.* martensite) was attributed to acicular ferrite. The difference in the intrinsic strength of acicular ferrite determined by both these methods corresponds to 85 MPa *i.e.* around 28 HV only.

CHAPTER 7

The Effect of Austenite Grain Size on Bainite Transformation Kinetics

The purpose of this work is to investigate the validity of the well known assumption that the austenite grain size affects the transformation kinetics of bainite, and to rationalise the nature of any observed effects. As will be seen later there are some good reasons for a reinvestigation on theoretical grounds.

7.1 Experimental Procedure

A steel was chosen of a suitable composition, given in Table 7.1, that would enable the kinetics of bainitic transformation to be observed without the interference of carbide precipitation. The presence of silicon greatly inhibits the formation of cementite). Isothermal reaction kinetics were measured by monitoring the dilatation of a sample using a Thermechmastor thermo-mechanical simulator. The kinetics are sufficiently slow in this steel for the time scale of the slight undershooting below the isothermal transformation temperature during quenching to be insignificant compared to the overall reaction time.

Alloy No.	С	Si	Mn	Ni	Мо	Cr	V
5763	0.16	2.00	1.46	0.02	-	-	-

Table 7.1 Composition of the steel used to investigate the effect of austenite grain size on the reaction kinetics of bainite. Composition values are in wt%.

Three different austenitisation treatments were applied in order to produce a large range of austenite grain sizes in the samples. After quenching to room temperature and tempering for 60 minutes at 600 °C the austenite grain structure of the specimens was examined using scanning electron microscopy and montage photographs containing numerous austenite grains were produced. The tempering process was applied with the object of enhancing the delineation of the prior austenite boundaries in the quenched microstructure (Yang, 1987). The grain size of the austenite was determined by deducing the mean linear intercept of a series of random lines with the outline of the austenite grains on these micrographs.

The isothermal heat treatment in the bainite temperature range was carried out on the three specimens after austenitisation at the different temperatures. The isothermal transformation temperature and cooling rate were identical for each sample, being set at 500°C and 40° Cs⁻¹ respectively. The specimens were mounted polished and etched in 2% nital before recording the microstructure using SEM.

It was also observed that the delineation of the austenite grains was more pronounced in the isothermally transformed specimens than in the specimens quenched to martensite and tempered. This enabled a measurement of the austenite grain size of the actual samples from which kinetic data were obtained. These results could then be compared with the values determined from the directly quenched martensitic specimens in order to confirm that the values agreed within the limits of experimental error.

The data of relative radius change, temperature and time were recorded in ASCII code and transferred from the thermomechanical simulator onto a SUN workstation for further analysis. Plots of relative radius change versus time were produced in order to compare the effect of the three different grain sizes on the transformation kinetics.

7.2 Results

Figures 7.1, 7.2 and 7.3 show micrographs of the samples austenitised for 3 minutes at 1300°C, 1200°C and 1000°C respectively. The grain size of the prior austenite is clearly markedly different in each specimen and as expected shows an increase as the austenitising temperature increases. Table 7.2 gives the mean linear intercept values determined for each sample in the quenched state. Figures 7.4, 7.5 and 7.6 show the microstructure of the specimens isothermally transformed at 500°Cfor 6 minutes. Figure 7.7 gives a comparison of the reaction profiles of these specimens, while Figure 7.8 confirms that the transformation kinetics at a lower temperature (480°Cfor 6 minutes) show similar results. Note that the time taken for transformation to approach its limiting value is greater than 100 s in all cases, whereas the duration of the undershooting below the isothermal transformation temperature is approximately 4 s.

Austenitisation Temp.	Mean Linear Intercept		
$T_{\gamma}/^{\circ}\mathrm{C}$	$\overline{L}/\mu\mathrm{m}$		
1300	$234\ \pm 30$		
1200	66 ± 7		
1000	36 ± 4		

Table 7.2 Mean linear intercept values for the prior austenite grain size of Alloy 5763, for three different austenitisation temperatures.

7.3 Discussion

As can be seen from Figures 7.7 and 7.8 the overall kinetics of transformation differ very little between samples of very different grain size. On the other hand, there is a marked



Figure 7.1 The microstructure of Alloy 5763 after austenitisation at 1300° C for 3 minutes followed by cooling at 40° Cs⁻¹ to room temperature. The microstructure is martensitic.



Figure 7.2 The microstructure of Alloy 5763 after austenitisation at 1200° C for 3 minutes followed by cooling at 40° Cs⁻¹ to room temperature. The microstructure is essentially similar to that shown in Figure 7.1



Figure 7.3 The microstructure of Alloy 5763 after austenitisation at 1000° C for 3 minutes followed by cooling at 40° Cs⁻¹ to room temperature. The microstructure has a fine austenite grain structure, clearly visible at this magnification



Figure 7.4 The microstructure of Alloy 5763 after austenitisation at 1300° C for 3 minutes followed isothermal transformation at 500° C to room temperature.



Figure 7.5 The microstructure of Alloy 5763 after austenitisation at 1200° C for 3 minutes followed isothermal transformation at 500° C to room temperature.



Figure 7.6 The microstructure of Alloy 5763 after austenitisation at 1000°C for 3 minutes followed isothermal transformation at 500°C to room temperature. The bainitic microstructure has a clearly defined prior austenite grain size.



Figure 7.7 Comparison of the reaction profiles obtained by thermomechanical simulator transformation of Alloy 5763 of three different γ grain sizes at 500°C. The reaction rate of the three specimens is shown to be very similar.



Figure 7.8 Comparison of the reaction profiles obtained by thermomechanical simulator transformation of Alloy 5763 of three different γ grain sizes at 480°C. The similarity in transformation kinetics for specimens of different grain sizes is again remarkable.

difference in the microstructure of the transformed specimens. The steels with the largest grain size, whose microstructure is shown in Figure 7.4, has extremely large sheaves, crossing the entire width of some grains. This is in contrast to the small grained specimen (Fig 7.6) in which the sheaves, while occasionally filling the grains, have a different appearance altogether, being shorter, and appearing to result from a greater number of separate grain boundary nucleation events. This results in more impingements between sheaves. It is interesting to note that the limiting relative radius change achieved depends on the austenite grain size of the specimen. While, for the two reaction temp[eratures investigated, the trend is not the same it is possible to speculate that this may be an effect due to the amount of blocky austenite trapped between large sheaves being greater in the case of the very large grained specimen. It is emphasised that the specimen with the largest grain size shows the smallest relative radius change at both transformation temperatures.

Simple considerations of grain boundary nucleated transformation products would suggest that the reaction rate of such phases would increase as the grain boundary area per unit increased. For martensite formation, however, it has been found that a decrease in the grain size depresses the martensite start temperature, when measured by comparatively insensitive techniques such as electrical resistance or dilatation (Cohen, 1991), despite the fact that the available sites for nucleation are expected to be more numerous for smaller grain sizes. More sensitive techniques such as acoustic emission actually reveal the opposite trend. These results can be rationalised by considering the volume of the product phase formed per grain boundary nucleation event. In martensite, where the plates tend to grow to the size of the parent grain, and autocatalysis effects can cause a burst of further transformation, the volume of ferrite formed per nucleation event is larger in the case of a larger grained specimen.

For the case of bainite, a rationalisation of the observed effect of grain size can be presented generally as follows. Consider the development of each individual sheaf. If the sheaf nucleates at time τ the normalised volume fraction of bainitic ferrite at that time is ξ , the normalisation is, as before, with respect to the appropriate limiting volume fraction. It is postulated that the possible number of sub-units which can grow within a sheaf is limited by a maximum value, denoted N_m . If N represents the number of sub-units in the sheaf at a given instant in time, then the rate of plate nucleation within a sheaf nucleated at time τ is

$$\frac{dN}{dt} = (1 - N/N_m) I\left\{\xi, N\right\}$$

where $I\{\xi, N\}$ where $I_{\xi,N}$ represents the nucleation rate of sub-units within the sheaf, which is a function of N and also of ξ , (since the extent of total transformation to ferrite will affect the austenite composition in which nucleation is occurring). The term $(1 - N/N_m)$ accounts for the extended volume effects on sub-unit nucleation, bringing nucleation to a stop when the sheaf has reached its limiting size.

The effect of autocatalysis can be expressed as follows

$$I\{\xi, N\} = (1 + \lambda_1 N) I_0\{\xi, N\}$$

where λ_1 is the autocatalysis constant for nucleation within a sheaf, and $I_0 \{\xi, N\}$ represents the nucleation rate independent of autocatalysis, which, due to effects like carbon enrichment of the austenite surrounding the sheaf, is also function of N. Therefore

$$\frac{dN}{dt} = I_0 \left\{ \xi, N \right\} \left(1 + \lambda_1 N \right) \left(1 - N/N_m \right)$$

The volume of a sheaf at a given time will be the multiple of the number of sub-units with the sub-unit volume u.

If the nucleation rate per unit volume at grain boundaries, (effectively, the nucleation rate of sheaves), denoted $I_{Sh} \{\xi\}$, is linearly dependent on the austenite grain surface per unit volume S_V it will be inversely dependent on the grain diameter represented by the mean linear intercept \overline{L} *i.e.*

$$I_{Sh} = I'_{Sh} / \overline{L}$$

where I'_{Sh} represents the contribution to I_{Sh} which is independent of the grain diameter. The nucleation rate is a function of the normalised volume fraction ξ of the bainite reaction.

Considering the overall transformation kinetics, the increment in volume fraction caused by the growth of a sheaf nucleated between τ and $\tau + d\tau$ is

$$\theta d\xi = \left((1-\xi) u I_{Sh} \left\{ \xi \right\} \int_{\tau}^{t} \left(\frac{dN}{dt'} \right) dt' \right) d\tau$$

therefore

$$\frac{d\xi}{d\tau} = \frac{I'_{Sh}\left\{\xi\right\}u(1-\xi)}{\theta \overline{L}} \int_{\tau}^{t} \left(\frac{dN}{dt'}\right)dt'$$

where θ is the maximum allowable extent of transformation, and as mentioned above

$$\frac{dN}{dt} = I_0 \left\{ \xi, N \right\} \left(1 + \lambda_1 N \right) \left(1 - N/N_m \right)$$

It is assumed that I_0 itself is a function of ξ since the degree of carbon enrichment of the untransformed austenite is likely to be different for sheaves nucleating at the beginning and at later stages of transformation.

Examination of these expressions indicates that the transformation kinetics can be affected in two ways by increasing the grain size of the transforming austenite. If the effect of increasing the maximum allowable size of a sheaf counteracts the diminished nucleation rate at the grain
boundaries then the increase in transformation kinetics with increasing grain size can be rationalised. Also to be considered however is the exact interplay between autocatalytic and grain boundary nucleation. If autocatalytic nucleation is much faster than the grain boundary process and dominates over it then the effect on kinetics of increasing the sheaf size is expected to dominate *i.e.* kinetics will increase since a much larger amount of ferrite can form very rapidly. If both nucleation rates are comparable, then the decrease in the grain size will enhance the grain boundary nucleation, with further nucleation of sheaves possible within the time taken for a sheaf to reach its limiting size. Under these conditions it would be expected that a smaller grain size would increase the transformation kinetics. A qualitative understanding of the observed phenomena is therefore possible but att present it is not possible to account for these effects in a quantitative manner.

CHAPTER 8

The Required Driving Force for Nucleation of Displacive Transformations

8.1 Introduction

The current technological importance of bainite and acicular ferrite is immense. Accurate modelling of the kinetics of these transformations is highly desirable for the purpose of alloy design. Understanding the thermodynamics of transformation is obviously vital in the modelling process.

Recent work has indicated that there are many important similarities between bainite and acicular ferrite. Advances in the understanding of the bainite transformation may therefore be applied to the acicular ferrite reaction. It is known that both acicular ferrite and bainite exhibit 'incomplete reaction' *i.e.* under isothermal conditions, the reaction is observed to cease well before the equilibrium, or paraequilibrium ferrite volume fraction has formed (Bhadeshia & Edmonds, 1979, 1980; Yang & Bhadeshia, 1987; Strangwood & Bhadeshia, 1987). Both phases also produce surface relief consistent with a macroscopic invariant plane strain (IPS) shape deformation (Strangwood & Bhadeshia, 1987), as well as occurring in both the 'upper' and 'lower' forms (Sugden & Bhadeshia, 1989). The essential difference between the phases lies in the fact that bainite nucleates on prior austenite grain boundaries, whereas acicular ferrite nucleates on non-metallic inclusions present in the steel. The inclusions are either trapped as oxides during the welding process, or are the result of deliberate additions made via the flux.

It has not, however, been established that the thermodynamic criteria for nucleation are identical for both phases, and since the location of nucleation events is different in the two cases, it is of great interest to investigate the effect that this may have on the thermodynamics of nucleation.

8.2 The Minimum Driving Force for Bainite Nucleation

It has been found that in general, the minimum required driving force for nucleation of bainite is a linear function of temperature (Bhadeshia 1981). It was also shown that the required driving force for the nucleation of Widmanstätten ferrite also follows the same relationship, indicating that the process of nucleation for these two phases is identical. The results suggest that during the nucleation of bainite carbon partitioning occurs, whereas during the growth process the transformation is diffusionless, with the carbon supersaturation being relieved after the formation of each bainitic sub-unit. The incomplete reaction phenomenon characteristic of bainite is a direct result of this transformation mechanism, since the plate formation stops

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when the untransformed austenite becomes sufficiently carbon-enriched to be unable to support further diffusionless transformation. Since acicular ferrite shows the same incomplete reaction phenomenon (Yang & Bhadeshia, 1987; Strangwood & Bhadeshia, 1987), it is assumed that its growth process is similar to that of bainite.

The fact that a linear relationship is observed between the driving force and the maximum temperature at which bainite formation can occur may be rationalised if it is considered that a minimum nucleation rate N is required for transformation to be observed. The relationship between N and the activation energy G^* can be expressed as follows

$$N = \nu \exp\left\{-\frac{G^*}{RT}\right\}$$

where ν is the attempt frequency. Transformation will begin once the undercooling below Ae_3 is sufficient to achieve the necessary driving force.

By rearrangement it is possible to show that the activation energy G^* is a linear function of temperature.

$$G^* = RT \ln \left\{ \frac{\nu}{N} \right\}$$

When the available driving force is plotted against the highest temperature at which displacive transformations are observed a linear relationship is obtained (Bhadeshia 1981). This observation suggests that the activation energy for bainite nucleation is also a linear function of driving force, making it consistent with the theory of isothermal martensite nucleation kinetics (Olson & Cohen, 1976).

8.2.1 The Nucleation of Acicular Ferrite

There has been considerable speculation concerning the nucleation mechanism of acicular ferrite on inclusions. It has been proposed the elastic stress fields around the non-metallic inclusions arising from differential thermal contraction during cooling could assist nucleation, or that plastic strains resulting from the thermal contraction around inclusions provide a source of nucleating defects, enabling displacive transformation to ferrite (Bhadeshia & Christian, 1990). It has already been proposed that grain boundaries provide defects for nucleation of bainite, but these defects obviously do not occur as a result of thermal contraction, since there is no difference in expansion coefficients betwen neighbouring grains. Other proposals for the nucleation mechanism for acicular ferrite include the suggestion that certain oxide structures can cause local decreases in carbon level, causing an increase in local driving force, thereby activating existing structural defects in the austenite matrix (Strangwood 1986). Another popular idea is that the 'lattice matching' between the inclusion and the ferrite determines why some inclusion species appear more potent as nucleating sites than others. Mills, Thewlis & Whiteman (1987) suggest that there may be a reproducible orientation relationship between the ferrite and the inclusion, though other experiments refute this suggestion (Dowling, Corbett & Kerr, 1986).

In all cases it is clear that the possibility exists for a significant difference in nucleation thermodynamics between acicular ferrite and bainite.

8.3 Experimental Procedure

Dilatometry was carried out using two pieces of apparatus, a THETA industries dilatometer (of the push rod variety) and a THERMECMASTOR thermo-mechanical simulator (TMS). A series of welds with systematic variations in deposit chemistry was provided by ESAB AB (Sweden). The compositions of these welds are given in Chapter 4, Table 4.1. Samples for dilatometry were prepared by cutting sections parallel to the weld centerline from the heart of each weld, well away from the areas of possible base plate dilution. These sections were hot swaged down to rods of the appropriate diameter. After homogenisation for three days at 1200 °C, in sealed quartz tubes under a partial pressure of argon, the outer layer of the rods was removed to eliminate any oxidised or decarburised surface. All specimens were nickel plated in order to minimise the possibility of decarburisation during austenitisation and surface nucleation during transformation. The specimen diameters for the THERMECMASTOR and the dilatometer were 6 mm and 3 mm respectively, with the respective lengths being 12 mm and 15 mm.

A characteristic of welding alloys with compositions similar to those in the experimental alloy series is that the kinetics of transformation to allotriomorphic ferrite are rather slow, resulting in as-deposited microstructures containing little or no allotriomorphic ferrite at prior austenite grain boundaries. Continuous cooling experiments at appropriate cooling rates can therefore be performed whilst completely avoiding all reconstructive transformations. The difference in the substitutional solute content of the weld metals does however require that faster cooling rates are applied to the lower alloy content variants, in order to avoid allotriomorphic ferrite formation.

Isothermal transformation experiments on these alloys indicate that the acicular ferrite reaction ceases in a matter of seconds. Combined with this is the fact that most predicted B_s temperatures for these alloys is nucleation limited *i.e.* the thermodynamic criterion for nucleation of bainite is satisfied at lower temperatures than the growth criterion. This criterion implies the presence of a flat-top lower C-curve in the TTT diagram for all steels in the alloy series. This is convenient for the present purposes since if the transformation-start temperature remains constant for two different cooling rates, then that temperature can be taken to represent the flat top. The cooling rates applied to the alloys over the temperature range of the lower C-curve were determined by the need to avoid reconstructive transformations whilst ensuring

that the cooling was sufficiently slow that transformation was detected at the highest possible temperature.

8.3.1 Austenite Grain Size

For acicular ferrite formation large austenite grains are required in order to reduce interference from the effects of grain boundary nucleated bainite. The dilatometer specimens were heat treated for 10 minutes at 1375°C to induce the growth of sufficiently large austenite grains. Such a treatment produces an extremely large grain size. Later work carried out on the TMS used an austenitisation treatment of 3 minutes at 1350°C, the shorter treatment being chosen to reduce the risk of decarburisation. Consistency between the microstructures produced by both treatments indicate that the grain size produced by the austenitisation treatment in the TMS was sufficient for intragranular effects to dominate those originating at the austenite grain surfaces.

Bainite formation requires the nucleation at grain boundaries to dominate over any intragranular nucleation. A small austenite grain size was therefore desirable for bainite formation. This was achieved by austenitising for 5 minutes at 1000 °C. Determination of the onset temperature was carried out on the TMS, since its superior vacuum system enabled the problem of decarburisation of the specimen surface to be eliminated. The earlier microstructural work carried out on the dilatometer showed that the transformation onset temperature increased as austenitisation times at high temperatures were increased. Observation of the microstructure of these specimens close to the surface confirmed that significant decarburisation had occurred. Microstructural observations on these specimens were therefore confined to central areas, well away from the surface.

Further precautions were taken to ensure that the problem of surface decarburisation was eliminated. The specimen chamber was purged with argon gas three times before pumping down to $\approx 2 \times 10^{-2}$ Pa prior to the austenitisation treatment. In the case of the high austenitisation temperature experiments with slower cooling rates, transformation was interrupted at an intermediate temperature in order to investigate the microstructure of the products formed at temperatures immediately below the onset temperature. By this method the location of transformation initiation could be determined more easily.

8.3.2 Determination of the Onset Temperature

Figure 8.1 shows schematically the procedure by which the transformation onset temperature was determined. The approximately linear contraction at higher temperatures indicates that no transformation is occurring. A straight line is fitted to this portion of the curve. Significant deviation from this straight line indicates the onset temperature of transformation



Figure 8.1 Schematic illustration of the method of determining the transformation onset temperature from dilatometric data.

 T_H .

8.3.3 Determination of the Required Driving Force for Nucleation

Using the theory outlined in Chapter 2 the values of ΔG_m , the maximum free energy change on nucleation were determined for the alloy compositions at the experimentally determined T_H values. These results were used to construct plots of ΔG_m versus T_H for nucleation in the large and small austenite-grained specimens, representing acicular ferrite and bainite respectively.

8.4 Results

Table 8.1 shows the transformation onset temperatures T_H observed after the different austenitisation treatments. The temperatures shown are the highest determined values from experiments with cooling rates between 5°Cs⁻¹ and 0.5°Cs⁻¹ for the lightly alloyed members of the series and between 0.5° Cs⁻¹ and 0.05° Cs⁻¹ for the more highly alloyed variants. Comparison between onset temperatures determined from more than one cooling rate was used to establish that the highest temperature of the lower C-curve was reliably established, and that slower cooling would not result in a higher onset temperature. Included in Table 8.1 are the values of ΔG_m corresponding to the transformation onset temperatures. A plot of ΔG_m versus T_H is displayed in Figure 8.2 in which both high-temperature and low-temperature austenitisation onset temperatures are shown.

Best fit lines were determined for the relationship between T_H and the driving force ΔG_m available at these temperatures. The regression equation for transformation to acicular ferrite is

$$\Delta G_m \{T_H\} = 3.112 \ T_H - 2163 \ \text{J mol}^{-1}$$

(for T_H specified in °C). The correlation coefficient for the best fit straight line was 0.967. The standard error for the regression coefficient and constant were 0.28 and 149 respectively.

For transformation to bainite, in the small-grained specimens, the regression equation was

$$\Delta G_m \{T_H\} = 3.127 \ T_H - 2153 \ \text{J mol}^{-1}$$

which has a correlation coefficient of 0.97. In this case the standard error in the regression coefficient and constant were 0.25 and 133 respectively.

Selected microstructures of the the transformed specimens are shown in Figures 8.4 to 8.10. The displayed micrographs reflect the different microstructures formed by the cooling processes, as a function of alloy content. For this purpose the high and low manganese variants of the alloy series, alloys 115 and 116 respectively, were singled out for examination. Table 8.2 gives the exact heat treatments experienced by the steels in each micrograph.

	$T_{\gamma} = 1$	1000°C	$T_{\gamma} = 1350^{\circ}\mathrm{C}$	
Alloy No.	T_H	ΔG_m	T_H	ΔG_m
112	563°C	-407	551°C	-472
113	$550^{\circ}\mathrm{C}$	-434	558°C	-390
114	510°C	-562	520°C	-507
115	480°C	-656	484°C	-634
116	570°C	-390	582°C	-325
117	511°C	-519	508°C	-524
118	568°C	-373	$564^{\circ}\mathrm{C}$	-395
119	520°C	-551	521°C	-545
120	552°C	-384	$526^{\circ}\mathrm{C}$	-526
121	514°C	-567	523°C	-522
122	540°C	-462	$556^{\circ}\mathrm{C}$	-375

Table 8.1 Transformation onset temperatures for the small-grained and largegrained specimens (*i.e.* the onset temperatures for transformation to bainite and acicular ferrite respectively). Also shown is the driving force at onset.

Figure No	Alloy	T_{γ}	Austenitisation Time	Cooling Rate	Apparatus
8.3	116	1375°C	10 min	$5^{\circ} \mathrm{Cs}^{-1}$	Dilatometer
8.4	116	$1350^{\circ}\mathrm{C}$	3 min	$0.5^{\circ} \mathrm{Cs}^{-1}$	TMS
8.5	115	1375°C	10 min	$5^{\circ} \mathrm{Cs}^{-1}$	Dilatometer
8.6	115	$1350^{\circ}\mathrm{C}$	3 min	$0.05^{\circ} \mathrm{Cs}^{-1}$	TMS
8.7	116	1000°C	5 min	$5^{\circ} \mathrm{Cs}^{-1}$	Dilatometer
8.8	116	1000°C	5 min	$0.5^{\circ} \mathrm{Cs}^{-1}$	Dilatometer
8.9	115	1000°C	5 min 5°Cs^{-1}		Dilatometer
8.10	115	1000°C	5 min	$0.05^{\circ} \mathrm{Cs}^{-1}$	Dilatometer

Table 8.2 Apparatus and austenite details of continuously cooled transformations.

8.5 Discussion

8.5.1 Onset Temperatures

The onset temperatures for reaction to acicular ferrite and bainite in the small grained specimens show the expected linear relationship between ΔG_m and T_H . It is interesting to note that the driving force versus onset temperature data for both acicular ferrite and bainite formation regress onto almost identical best-fit straight lines, despite the fact that the individual alloys show small changes in T_H following the different austenitisation treatments. There is no systematic trend in these small variations. Also noteworthy is the close agreement between the determined regression equations and that obtained by Ali & Bhadeshia (1990) from the data of Steven & Haynes *i.e.*

$$G_N = 3.636 \ T_H - 2540 \ \mathrm{J} \ \mathrm{mol}^{-1}$$

The discrepancy between the two expressions, indicated in Figure 8.2, suggest that it is somewhat easier to nucleate displacive transformations in the welding alloys than in the steels studied by Steven & Haynes. A possible reason for this is that the low carbon content of the alloys studied here results in lower solid solution strengthening of austenite by carbon in the bainite transformation temperature range. Lower austenite yield strength would ease the motion of interface dislocation motion during displacive transformation (Olson & Cohen, 1976). Isolating the lowest carbon steels used by Steven & Haynes for special consideration (compositions are given in Table 8.3), it is interesting to note that the driving force at the reported B_S temperatures of these steels is consistently lower than that predicted by the overall relationship between ΔG_M and B_S , determined by considering the complete set of steels, some of which were of much higher carbon content. Figure 8.11 illustrates the driving force at the reported B_S temperature for these steels lie between the curves representing overall relationship from data of Steven & Haynes and the curve determined for the welding alloys outlined in this chapter. It has been reported (Irvine, Llewellyn & Pickering, 1961) that the solid solution strengthening of austenite by carbon is much potent than that of substitutional alloying elements, therefore it is plausible that the effect of carbon on the required driving force for nucleation of displacive transformation is noticable over and above its effect of the thermodynamics of the austenite \rightarrow ferrite phase change.

С	Si	Mn	Ni	Mo	\mathbf{Cr}	$B_S/^{\circ}\mathrm{C}$	$\Delta G_m/{ m J}~{ m mol}^{-1}$
0.19	0.14	1.37	0.56	0.31	0.2	600	-348
0.14	0.19	0.46	3.55	0.12	1.11	550	-444
0.15	0.25	0.41	3.02	0.15	0.9	580	-362
0.11	0.21	0.3	5.04	0.3	0.13	550	-428
0.15	0.2	0.38	4.33	0.17	1.16	500	-634
0.14	0.22	0.5	2.13	0.18	2.00	520	-644
0.19	0.21	0.90	1.87	0.18	1.08	530	-617

Table 8.3 Alloy compositions and driving force values at B_S for the lowest carbon alloys used by Steven & Haynes (1956).

8.5.2 Microstructure

The micrographs of the high-temperature austenitisation specimens are shown in figures 8.3 to 8.6, with those for low temperature austenitisation shown in figures 8.7 to 8.10. Figure 8.3 (a) and (b) shows the microstructure of alloy 116 cooled to room temperature at $5^{\circ}Cs^{-1}$ after austenitisation at 1375°C. The higher magnification image clarifies the dense microstructure, showing the very high volume fraction acicular ferrite structure. The same alloy, cooled more slowly and interrupted by quenching at 450°C indicates the uniform formation of acicular ferrite plates (Figure 8.4). In comparison, the alloy 115 specimen cooled at $5^{\circ}Cs^{-1}$ shown in Figure 8.5 indicates a greater tendency to form intra-granularly nucleated sheaves, and display a smaller fraction of transformation. Cooling alloy 115 at $0.05^{\circ}Cs^{-1}$ and interrupting the cooling by quenching from 400°C reveals very large sheaves in surrounded by large regions of martensite as shown in Figure 8.6.

In contrast to the large austenite grained specimens, the transformation resulting form the low temperature austenitisation was invariably to bainite, though 'granular bainite' was observed at slower cooling rates. Granular bainite does not of course differ from conventional bainite in transformation mechanism, but is a morphological variant which is a consequence of the slow continuous cooling transformation. Figure 8.7 and 8.8 shows the bainitic structures of alloy 116 cooled at 5° Cs⁻¹ and 0.5° Cs⁻¹ respectively. The fraction of transformation is so high that it is difficult to identify individual sheaves. In contrast, the microstructures of the small austenite-grained alloy 115 specimens (Figure 8.9 and 8.10 respectively) show more recognisable sheaves though the specimen cooled at 0.05° Cs⁻¹ exhibits a granular bainite structure.

These metallographic results can be rationalised by considering the nucleation rates of the alloys at the early stages of transformation. In the coarse grained specimens grain boundary nucleation is all but eliminated, nucleation of acicular ferrite on inclusions being dominant. The more slowly cooled specimens yield the most interesting findings. In the lightly alloyed steel the nucleation rate is high resulting in a uniform distribution of individual plates acicular ferrite. Slower cooling would result in allotriomorphic ferrite formation. In the more highly alloyed steel at very slow cooling the nucleation rate at the onset of transformation is small resulting in the greater importance of auto-catalytic nucleation, hence the presence of intragranularly nucleated sheaves (Fig. 8.6). At higher cooling rates the development of sheaves in inhibited but the rapidly increasing driving force causes further nucleation and results in more hard impingement between plates. The resulting microstructure therefore consists of a fine dispersion of plates showing lower tendency to form sheaves (Fig. 8.5).

In the small grained specimens, the increased grain boundary nucleation rates result in bainitic structures. It is notable again that the formation of recognisable sheaves is more pronounced in the solute-rich alloy 115 which presumably has a lower nucleation rate at the grain boundaries. Granular bainite structures result from the condition in which the extent of transformation is always at its maximum allowable value during the slow cooling. The redistribution of partitioned carbon under these circumstances is enhanced, resulting in the obvious martensitic regions in the microstructures.

8.6 Conclusions

It can be seen from Figure 8.2 that the linear relationship between the driving force required for a detectable rate of nucleation is displayed by the experimental welding alloys for transformation to both acicular ferrite and bainite. This result is significant since it corresponds closely to the published relationship between driving force and onset temperature observed in transformation to Widmanstätten ferrite, and bainite. Acicular ferrite is therefore concluded to nucleate by a similar mechanism to these two phases. It would appear that the mechanism of acicular ferrite nucleation most consistent with these results is that dislocation arrays produced by thermally induced plastic strains around inclusion particles act as the necessary defects which develop into acicular ferrite nuclei. Such a mechanism is consistent with the fact that both acicular ferrite and bainite nucleate under apparently identical thermodynamic conditions. If nucleation around inclusions were stress-assisted, such close agreement between required driving force for acicular ferrite and bainite nucleation would be merely coincidental, since such stresses are not present at grain boundaries. Similarly, for the proposed case of lattice matching at the inclusion/ferrite interface, the similarity in the required driving force for acicular ferrite and bainite, despite the fact that the interface characteristics were very different, would not be expected. The possibility of chemical interaction at the inclusion/austenite interface is again inconsistent with the present findings.

The proposed strain-assisted mechanism for nucleation is consistent with the present findings since it suggests the creation of new, active defects around inclusions which operate in the same way as defects at grain boundaries which give rise to bainite nuclei. The difference in nucleation potency between different chemical species of inclusions is then probably the result of the different amount of plastic strain occurring around the particles during cooling, since the relative thermal contraction between the inclusions and austenite will vary with inclusion species.

The observed microstructures indicate the important role played by the cooling rate in the eventual structure of displacively transformed specimens. High nucleation rates, both on grain boundaries and on inclusions lead to sheaf formation being stifled. In granular bainitic structures the regions left untransformed after cooling to room temperature are more noticeable since the slow cooling rates enable complete redistribution of partitioned carbon resulting in a smaller fraction of trapped carbon between bainitic sub-units.



Figure 8.2 A plot of driving force ΔG_m versus reaction onset temperature for transformation to acicular ferrite (large prior austenite grains) and to bainite (small prior austenite grains). For comparison purposes, the relationship between ΔG_m and T_H derived from the data of Steven & Haynes (1956) is included, indicating that the welding alloys considered require a somewhat lower driving force for nucleation.



Figure 8.3 The microstructure of alloy 116, austenitised for 10 min. at 1375° C, cooled at 5° Cs⁻¹. a) low magnification image b) high magnification image showing the acicular ferrite structure.



Figure 8.4 The microstructure of alloy 116, austenitised for 3 min. at 1350° C, cooled at 0.5° Cs⁻¹. The transformation was interrupted by quenching at 450° C.



Figure 8.5 The microstructure of alloy 115, austenitised for 10 min at 1375° C, cooled at 5° Cs⁻¹.



Figure 8.6 The microstructure of alloy 115, austenitised for 3 min at 1350° C, cooled at 0.05° Cs⁻¹. The transformation was interrupted by quenching at 400° C.



Figure 8.7 The microstructure of alloy 116, austenitised for 5 min at 1000°C, cooled at $5^{\circ}Cs^{-1}$.



Figure 8.8 The microstructure of alloy 116, austenitised for 5 min at 1000°C, cooled at 0.5° Cs⁻¹.



Figure 8.9 The microstructure of alloy 115, austenitised for 5 min at 1000°C, cooled at $5^{\circ}Cs^{-1}$.

Figure 8.10 The microstructure of alloy 115, austenitised for 5 min at 1000°C, cooled at 0.05° Cs⁻¹.



Figure 8.11 A plot of the driving force at the highest temperature at which displacive transformations are observed in the lowest carbon steels considered by Steven & Haynes (1956). Also included are the best fit lines representing the driving force at B_S for the welding alloys, and the overall relationship from the data of Steven & Haynes.

CHAPTER 9

Microstructure and Properties of Isothermally Transformed High Strength Weld Metals

9.1 Introduction

The aim of work presented in this chapter was to consolidate and apply the results presented in the earlier chapters of the thesis. Thus, the kinetics of acicular ferrite formation were investigated as a function of alloy chemistry and isothermal transformation temperature. At the same time an attempt was made to rationalise the morphology and strength of the resulting mixed acicular ferrite and martensite microstructures. The data were also interpreted in terms of the thermodynamics and mechanism of acicular ferrite reaction.

Homogenised samples of reaustenitised weld metals were isothermally transformed to investigate the following:

- (a) The kinetics of acicular ferrite formation in reaustenitised weld metal of different chemical compositions. The effect of temperature was also considered.
- (b) The morphology of acicular ferrite changes as a function of driving force and active nucleation site density. The aim was to rationalise of the microstructures observed in isothermally transformed specimens.
- (c) Martensite and acicular ferrite have different properties. The strength and hardness of the mixed microstructures should therefore be dependent on the amount of acicular ferrite present. The fraction of each microstructural component was measured for isothermally transformed and quenched samples. Mean hardness values from each specimen were then correlated with the measured acicular ferrite content and the alloy chemistry. The yield strength of a mixed microstructure of acicular ferrite and martensite is expressed as

$$\sigma_y = V_{\alpha_a} \left(\sigma_{Fe} + \sum_i x_i \kappa_i + \Delta \sigma_{\rm mic} \right) + (1 - V_{\alpha_a}) \sigma_{\alpha'}$$

(where the notation is the same as in Chapter 6). The microstructural contribution of acicular ferrite to the overall hardness $\Delta \sigma_{\rm mic}$ was determined, and the agreement between predicted and measured hardness was examined.

(d) The maximum amount of acicular ferrite that can form at any temperature increases with undercooling below the B_S temperature (Yang & Bhadeshia, 1987). The variation is expected to be consistent with the slope of the T'_0 curve in the phase diagram. The measured volume fraction of acicular ferrite was compared with calculations for each alloy.

9.2 Experimental Method

Specimens of weld metal were cut from the undiluted heart of each weld and swaged down to 8 mm diameter rods. The rods were homogenised by sealing in quartz tubes under a partial pressure of pure argon and holding for 3 days at 1200°C before water quenching. The outer layers of the rods were then removed by turning down to a diameter of 6 mm. Dilatometry was carried out on a THERMECMASTOR thermo-mechanical simulator (TMS). A large austenite grain size was required in order to enhance the formation of acicular ferrite. An austenitisation treatment of 1 minute at 1350°C was found to be adequate in this respect, with little or no grain boundary nucleated bainite being observed in the transformed specimens. After austenitisation the specimens were cooled to the isothermal transformation temperature at 40° Cs⁻¹ and held there for five minutes before quenching to room temperature with nitrogen gas. This was found to give the optimum compromise cooling rate that minimised the undershooting of the isothermal hold temperature whilst at the same time ensured the absence of transformation during the quench. As will be explained later, the undershooting of the test temperature on cooling *did* prove to be a major obstacle in producing accurate quantitative data for the early stages of transformation. For scanning electron microscopy, specimens were cut, mounted and polished using standard metallographic techniques, then given a medium/deep etch in 2% nital. Hardness testing was performed using a Vickers pyramidal indenter (load 10 kg) on lightly etched samples. The mean of five measurements was taken for each sample.

9.3 Results

Figures 9.1-9.3 show the dilatometric results from isothermal transformation experiments at a variety of temperatures, for each alloy in the high strength weld metal series. The figures show plots of relative radius change, $\Delta r/r$ versus time. Examples of the acicular ferrite morphology in the transformed specimens are shown for alloys 118 and 115 in Figures 9.4-9.6 and Figures 9.7-9.9 respectively. Alloy 118 is the low nickel variant of the alloy series, with alloy 115 being the high manganese variant. These alloys were selected for display since they most clearly illustrate the trends in microstructure shown by the welding alloys as the transformation temperature was varied. In Figures 9.10, 9.11 and 9.12, the experimentally measured volume fractions of acicular ferrite observed in the transformed specimens are compared with theory, assuming transformation stops when the austenite carbon content reaches $x_{T'_0}$. The $x_{T'_0}$ composition was determined using theory outlined in Chapter 2. A comparison of the predicted and experimentally measured hardness values (after optimising the microstructural strength contribution of acicular ferrite to the overall specimen hardness was found to be

$$\Delta \sigma_{\rm mic} = 352 \pm 20 \text{ MPa} \tag{9.1}$$

9.4 Discussion

9.4.1 Transformation Kinetics

It must be noted that after quenching, the duration of the undershoot below the desired isothermal transformation temperature was around 4 seconds on average, meaning that the results shown in Figures 9.1-9.3 are not truly representative of the early stages of the transformation since ferrite formation and thermal expansion are occurring simultaneously. It proved impossible to fit the transformation data to the model presented in Chapter 3, the disagreement between prediction and experiment at the early stages of transformation dominating the error, resulting in poor overall agreement, and unsatisfactory determination of the empirical constants of the model. In all the isothermal runs the relative radius change reading decreased momentarily shortly after it reached its maximum value, as can be seen clearly in some of the experimental data. The magnitude of this effect was not identical in all specimens, nor did it always occur at the same time. Examination of the microstructures of the transformed specimens showed little change across the specimen diameter, suggesting that if this effect was due to thermal contraction of the specimen core, which was at a higher temperature than the exterior during transformation, the effect on the resultant microstructure was negligible. It is conceivable however, that the transformation rate of the core region might differ from that of the exterior if such temperature gradients did exist in the specimen.

It is noteworthy that the transformation rates of all alloys are similar, depending mainly on the undercooling of each alloy below its respective B_S temperature, despite the fact that the predicted B_S temperatures themselves vary by around 70°C (*c.f.* alloy 114 and alloy 116). If W_S represents the highest temperature at which nucleation of bainite is possible, and that at this temperature there is a minimum nucleation rate, the kinetics of transformation to bainite or acicular ferrite are determined primarily by the undercooling below W_S . (In most of the welding alloys considered here W_S and B_S are identical *i.e.* transformation is nucleation limited.) The observation that at similar undercooling below W_S the reaction kinetics are similar for all the welding alloys, despite differences in substitutional solute content, supports the assertion that all alloys have the same nucleation rate at W_S (Bhadeshia 1981a). It is therefore also consistent with the modified bainite kinetics model presented in Chapter 3. The small differences in the carbon contents of the alloys ensure that autocatalytic effects are similar despite their different substitutional solute content.

9.4.2 Morphology of Acicular Ferrite in Isothermal Transformed Specimens

The isothermal transformation temperatures used were chosen in order to investigate the nature of acicular ferrite formation at small driving forces and therefore low nucleation rates. It is interesting to note that at the smallest undercoolings (Figures 9.6 and 9.9) both alloy 118

and alloy 115 show a marked tendency for sheaf formation, which decreases somewhat as the driving force increases. Undoubtedly, at low driving forces, the significance of each nucleation event on an inclusion is increased, enabling subsequent auto-catalytic nucleation to dominate the eventual microstructure, since when nucleation rate is low there is less impingement between plates nucleated on neighbouring sites. Since the auto-catalytic nucleation occurs on previously formed plates, it is reasonable to assume that, given the opportunity, the plates will align in a manner similar to bainite sheaves. At higher driving forces (Figures 9.4, 9.5, 9.7 and 9.8) when the nucleation frequency is higher, the resulting hard impingement between plates stifles sheaf formation, though alloy 118 transformed at 500 °C continues to show some sheaves (Figure 9.4). Transformed at 450°C alloy 115 shows a conventional acicular ferrite microstructure.

The apparent variation of plate size in the microstructure of alloy 118 transformed at 500°C and 510°C (Fig. 9.4 and 9.5) is probably due to sectioning effects on plate arrays that show a high degree of alignment, suggesting that certain plate orientation variants are favoured.

The very clear contrast between the acicular ferrite and the inter-plate regions is probably due to the fact that during the isothermal transformation hold (5 minutes) there was ample time for complete carbon redistribution in the untransformed austenite, resulting in clear etching differences between the acicular ferrite and the subsequently formed martensite. It is possible that the inter-plate regions observed in the microstructure of alloy 118 transformed at 530 °C (Fig. 9.6) contain a fine dispersion of acicular ferrite plates, since carbon enrichment of the untransformed austenite would not have occurred to a great degree with such a small volume fraction of acicular ferrite being formed. The retardation of the acicular ferrite reaction by the partitioned carbon would therefore not be sufficient to prevent transformation during the post-isothermal hold quench. There is, however, no difficulty in distinguishing the acicular ferrite formed at the isothermal hold temperature from the inter-plate regions in the eventual microstructure.

Since it is believed that sheaves offer less resistance to crack propagation than dispersions of plates, as in acicular ferrite, the implications these results have for isothermally transformed inoculated steels are clear. If a fine, uniform acicular ferrite microstructure with a large fraction of martensite is desired this can best be achieved by partial transformation to acicular ferrite at a relatively low temperature *i.e.* interrupting the transformation before completion by quenching, rather than allowing complete transformation to the maximum allowable extent at a higher temperature at which sheaf formation tendency will increase.

9.4.3 Properties of Isothermally Formed Acicular Ferrite/Martensite Structures

The degree of agreement between the predicted and measured hardness of the isothermally transformed specimens supports the applicability of the model described in Chapter 6 for predicting the hardness of mixed microstructures of acicular ferrite and martensite. Since the plate size of acicular ferrite and the sheaf morphology is slightly different in continuously cooled and isothermally transformed specimens it is unlikely that the microstructural strengthening component of acicular ferrite is the same in both cases. It must be noted however that there is also likely to be a variation in this term for specimens of each alloy transformed at different temperatures, since it is driving force differences that give rise to variations in plate size and sheaf forming tendency.

The best fit value for the microstructure strengthening term was however very close to the value determined in Chapter 5 for the as-deposited weld metals. When this optimised term is included in the model for overall hardness of the microstructure there is fair agreement between predicted and experimental results (Figure 9.13). The large amount of scatter in the results is perhaps a consequence of certain microstructures where, due to the low fraction of acicular ferrite formed during the isothermal hold, the formation of further small amounts of ferrite during the quench to martensite was unavoidable. In the point counting procedure, the areas obviously formed during isothermal treatment were counted as acicular ferrite and other regions classed as martensite, though in fact the martensite may be interspersed with fine acicular ferrite plates formed during the post isothermal-hold quench *e.g.* Figure 9.6. The small fractions of fine acicular ferrite formed during quenching could conceivably affect the overall hardness of the microstructure.

9.4.4 The Incomplete Reaction Phenomenon in Acicular Ferrite

As can be seen from Figures 9.10, 9.11 and 9.12 the measured volume fraction of acicular ferrite decreases dramatically as the B_S temperature is approached. This is despite the fact the transformation temperature is well inside the $\alpha + \gamma$ phase field. It is clear that the transformation mechanism is far from equilibrium. The acicular ferrite fractions formed by isothermal transformation are significantly lower than that predicted by assuming that reaction stops when the carbon content of the untransformed austenite reaches $x_{T'_0}$ or x_{N_0} . This discrepancy lies outside the statistical error limit of the volume fraction measurements ($\approx 10\%$) and even if it is assumed that acicular ferrite contains no carbon, the measured ferrite volume fraction of acicular ferrite still falls below the predicted value. Note that this is despite the fact that, as shown in Chapter 8, the steels are observed to transform to acicular ferrite and bainite above the predicted B_S temperatures, as is confirmed by certain isothermal transformation results presented here. In such cases the measured volume fraction is obviously greater than the predicted value.

Undershooting the isothermal transformation temperature might also be expected to increase the amount of acicular ferrite by boosting nucleation at the earlier stages of transformation. The measured acicular ferrite fractions of acicular ferrite are lower than theory predicts despite this effect as well.

A possible reason for the phenomenon is that the build up of stresses in the austenite around plates of acicular ferrite hinders the late stages of transformation. This is despite the fact that indications are that it is easier to nucleate acicular ferrite and bainite in these welding alloys than in conventional wrought steels, as discussed in Chapter 8.

9.5 Conclusions

The kinetic data from isothermal transformation of the high strength welding alloys supports the theoretical prediction that the rate of reaction is determined mainly by the undercooling below the B_S temperature. Quantitative optimisation of a model for acicular ferrite kinetics was not possible since the undershooting of the isothermal transformation temperature interfered with the dilatometric data at early stages of transformation.

The microstructure of the isothermally transformed specimens illustrates the importance of driving force on the development of sheaves from the initial nucleation events on inclusions. At higher driving forces the tendency to form sheaves decreases. The extent of transformation measured in the the experimental specimens indicates that the prediction of the limiting acicular ferrite volume fraction using the $x_{T'_0}$ curve is a consistent overestimate.

Prediction of the hardness of microstructures consisting of a mixture of acicular ferrite and martensite by estimating the contributions of the microstructural constituents to the overall hardness is found to be in broad agreement with the measured values.



Figure 9.1 Isothermal transformation kinetics data for (a) alloy 112 (b) alloy 113 (c) alloy 114 (d) alloy 115. The transformation temperatures of each run are indicated on the plots.



Figure 9.2 Isothermal transformation kinetics data for (a) alloy 116 (b) alloy 117 (c) alloy 118 (d) alloy 119. The transformation temperatures of each run are indicated on the plots.





Figure 9.3 Isothermal transformation kinetics data for (a) alloy 120 (b) alloy 121 (c) alloy 122. The transformation temperatures of each run are indicated on the plots.



Figure 9.4 The microstructure of alloy 118 isothermally transformed for five minutes at 500° C after austenitisation for 1 minute at 1350° C. Acicular ferrite plates appear raised, and are clearly distinguishable from surrounding martensite.



Figure 9.5 The microstructure of alloy 118 isothermally transformed for five minutes at 510°C after austenitisation for 1 minute at 1350°C. The acicular ferrite shows an increased tendency to form sheaves (arrowed).



Figure 9.6 The microstructure of alloy 118 isothermally transformed for five minutes at 530° C after austenitisation for 1 minute at 1350° C. Sheaf formation is very pronounced.



Figure 9.7 The microstructure of alloy 115 isothermally transformed for five minutes at 450° C after austenitisation for 1 minute at 1350° C. The tendency to form sheaves is slight.



Figure 9.8 The microstructure of alloy 115 isothermally transformed for five minutes at 460°C after austenitisation for 1 minute at 1350°C. There is a profound increase in sheaf forming tendency (arrowed), and some plate orientations appear favoured.



Figure 9.9 The microstructure of alloy 115 isothermally transformed for five minutes at 470° C after austenitisation for 1 minute at 1350° C. The acicular ferrite fraction is very low, therefore sheaf formation is pronounced (arrowed).



Figure 9.10 Comparison of predicted and measured volume fractions of acicular ferrite for different isothermal transformation temperatures: (a) alloy 112 (b) alloy 113 (c) alloy 114 (d) alloy 115.



Figure 9.11 Comparison of predicted and measured volume fractions of acicular ferrite for different isothermal transformation temperatures: (a) alloy 116 (b) alloy 117 (c) alloy 118 (d) alloy 119.





Figure 9.12 Comparison of predicted and measured volume fractions of acicular ferrite for different isothermal transformation temperatures: (a) alloy 120 (b) alloy 121 (c) alloy 122


Figure 9.13 Comparison of predicted and experimentally measured hardness values of the isothermally transformed specimens from the welding alloy series.

CHAPTER 10

Future Work

10.1 Further Application of Present Work

Many of the experimental and theoretical tools developed during this work can be applied in a general way to other materials and under different conditions. Computer algorithms have been developed that will enable the analysis of new data on bainite kinetics and optimisation of the model refined during the course of this study. In this way it will be possible to identify trends previously unaccounted for, which will stimulate further research in the field. It has also been demonstrated that use of SEM enables more meaningful quantification of high strength microstructures, which will aid the improvement of quantitative models of microstructure development and mechanical properties.

10.2 New Work

Many topics which would be essential to and eventual comprehensive model of weld microstructure development have not been considered. The quantitative analysis of the continuous cooling transformation to acicular ferrite is an example. In principle it is possible to analyse the dilatometric data obtained during continuous cooling to give volume fraction data versus time and temperature. Computer programs have been developed to analyse the data and determine best fit constants for the bainite model under these conditions. Difficulties arise however in accounting for the variation in the expansion coefficient of austenite with cooling rate. It would certainly be of interest however to identify trends in the microstructures produced in the alloys considered in this work under fast cooling conditions.

Extraction replica TEM work would enable the analysis and quantification of the inclusion content and size distribution in the weld metal. In the absence of other contributory factors this inclusion distribution will have and important effect on the nucleation rate of acicular ferrite. It will be of great interest to investigate whether the measured compositions of the active inclusions support the conclusions of recent work at Cambridge on the mechanism of nucleation on inclusions (Gregg, 1992).

Analysis of Dilatometric Data

Data from the dilatometer and thermo-mechanical simulator is output as relative length change $\Delta l/l$ (or relative readius change $\Delta r/r$), temperature and time. In order to monitor the development of the ferrite volume fraction during isothermal transformation it is necessary to analyse the length change data.

Let a_{α}, a_{γ} and $a_{\overline{\gamma}}$ represent the lattice parameter of carbon-free ferrite, austenite of a carbon mole fraction x_{γ} and austenite of bulk alloy carbon mole fraction \overline{x} . Assuming isotropic dilatation in a polycrystalline test specimen, the relative length change (or relative radius change) can be related to the relative volume change $\Delta V/V$

$$\frac{\Delta V}{V} = \frac{\Delta l}{l} + 2\frac{\Delta r}{r} = 3\frac{\Delta l}{l}$$

After a volume fraction V_{α} of ferrite has formed

$$\frac{\Delta l}{l} = \frac{2V_{\alpha}a_{\alpha}^3 - (1 - V_{\alpha})a_{\gamma}^3 - a_{\overline{\gamma}}^3}{3a_{\overline{\gamma}}^3}$$

The lattice parameter of austenite is calculated in the following way

$$a_{\gamma} = \left(a_0 + c_c x_{\gamma} + \sum_j c_j x_j\right) \left(1 + e_{\gamma}(T - 298)\right)$$

where

$$x_{\gamma} = \frac{\overline{x} - V_{\alpha} x_{\alpha}}{1 - V_{\alpha}}$$

and

$$a_{\gamma} = \left(a_0 + c_c \overline{x} + \sum_j c_j x_j\right) \left(1 + e_{\gamma} (T - 298)\right)$$

where a_0 is the lattice parameter of unalloyed austenite at room temperature, and c_c and c_j are the coefficients of contributions to lattice parameter of carbon and the *i*th substitutional alloying element.

The lattice parameter of ferrite at the reaction temperature is

$$a_{\alpha} = a_{\alpha 0} \left(1 + e_{\alpha} (T - 298) \right)$$

where $a_{\alpha 0}$ is the experimentally measured lattice parameter of carbon-free ferrite. e_{γ} and e_{α} are the experimentally determined linear thermal expansion coefficients of austenite and ferrite respectively. The equation relating $\Delta l/l$ with V_{α} can then be solved iteratively for each value of $\Delta l/l$, thereby describing the development of ferrite during the isothermal hold.

	Fe-Mn-Si-C	Fe-Ni-Si-C	300 M
e_{α}	$0.13049 \times 10^{-4} K^{-1}$	$0.11826 \times 10^{-4} K^{-1}$	$0.11103 \times 10^{-4} K^{-1}$
e_{γ}	$0.21151 \times 10^{-4} K^{-1}$	$0.18431 \times 10^{-4} K^{-1}$	$0.17591 \times 10^{-4} K^{-1}$
$a_{\alpha 0}$	$2.8869 \pm 0.002 ~\rm{\AA}$	$2.8650 \pm 0.0016 ~\rm{\AA}$	$2.8661 \pm 0.001 ~\rm{\AA}$

Bhadeshia (1982b) obtained the following values for e_{α} , e_{γ} and $a_{\alpha 0}$ for the three high-silicon steels used in his analysis of the isothermal transformation kinetics of bainite.

Program for Optimisation of Bainite Kinetics Constants

PROGRAM MAIN IMPLICIT DOUBLE PRECISION (A-H,L-Z), INTEGER (I-K) DIMENSION CNT(4), IND(50) * junk is a disposable output file, wa contains the initial guess values * for the constants. RTOT is the current best sum of squares error. OPEN (UNIT=1,FILE='wa') open (unit=3,file='theory/geff6/junk') ILIM=1CALL IDENTIFY(IND,ID) READ (1,*) (CNT(J1),J1=1,4),RTOT WRITE (3,*) CNT(4)CALL MINIMISE(CNT, RTOT, IND, ID, ILIM) END * This subroutine identifies the individual dataruns in the * set and arranges them in a two dimensional array IDENTIFY (INDR, IDR) IMPLICIT DOUBLE PRECISION (A-H,L-Z), INTEGER (I-K) COMMON /ONE/ TKI(75,50), VNI(75,50), TIMI(75,50), THI(75,50) COMMON /TWO/ FMI(75,50),NDI(75,50),WSI(75,50),XBI(75,50) DIMENSION INDR(50) IDR=1 IVDR=0 PRE=0.0d0DO 10 I1=1,5000 $J_{2=0}$ READ (5,*,END=11) AA,BB,CC,DD,EE,FF,GG,HH IF (BB.GT. PRE) THEN IF (I1 .EQ. 1) IVDR=0 IVDR=IVDR+1 PRE=BB ELSE PRE=0.0IDR=IDR+1 IVDR=1 ENDIF VNI(IDR,IVDR)=AA TIMI(IDR, IVDR)=BB THI(IDR, IVDR)=CC FMI(IDR, IVDR)=DD TKI(IDR, IVDR)=EE NDI(IDR, IVDR)=FF

10 11	WSI(IDR,IVDR)=GG+273.15 XBI(IDR,IVDR)=HH INDR(IDR)=IVDR CONTINUE INDR(IDR)=IVDR
	END
* This * favou	subroutine adjusts the constants in turn and adopts any rable changes
	MINIMISE(CNT,TOT,IMND,IMD,ILIM) IMPLICIT DOUBLE PRECISION (A-H,L-Z),INTEGER (I-K) COMMON /ONE/ TKM(75,50),VNM(75,50),TIMM(75,50),THM(75,50) COMMON /TWO/ FMM(75,50),NDM(75,50),WSM(75,50),XBM(75,50) DIMENSION CNT(4),CDUM1(4),CDUM2(4),IMND(50) IIT=0 IGO=0 DO 10 IDUM=1,4 CDUM1(IDUM)=CNT(IDUM) CDUM2(IDUM)=CNT(IDUM)
10	CONTINUE
1	DO 30 I1=1,4
2	PARA=0.3D0 CDUM1(II)=(1.0D0+PARA)*CNT(II) CDUM2(II)=(1.0D0-PARA)*CNT(II) CALL SUMSQ(CDUM1,SUM1,IMND,IMD,IGO) CALL SUMSQ(CDUM2,SUM2,IMND,IMD,IGO) IF (SUM1 .LT. TOT) THEN TOT=SUM1 CNT(II)=CDUM1(I1) WRITE (3,999) (CNT(J1),J1=1,4),TOT IIT=IIT+1 IF (IIT .GE. ILIM) GOTO 31 ENDIF IF (SUM2 .LT. TOT) THEN TOT=SUM2 CNT(II)=CDUM2(II) WRITE (3,999) (CNT(J1),J1=1,4),TOT IIT=IIT+1 IF (IIT .GE. ILIM) GOTO 31 ENDIF IF (PARA .GT. 1.0D-07) THEN PARA=0.3D0*PARA GOTO 2
30	ENDIF
31	IF (IIT .LE. ILIM) THEN
	GOTO 1
	LDF

999	IGO=1 CALL SUMSQ(CNT,SUM1,IMND,IMD,IGO) ENDIF FORMAT (' ',5D15.5) END
* This s * predic	soubroutine calculates the sum of squares error between the sted and measured reaction times
	SUMSQ(CD,SUMM,ISND,ISD,IGO) IMPLICIT DOUBLE PRECISION (A-H,L-Z),INTEGER (I-K) COMMON /ONE/ TKS(75,50),VNS(75,50),TIMS(75,50),THS(75,50) COMMON /TWO/ FMS(75,50),NDS(75,50),WSS(75,50),XBS(75,50) DIMENSION CD(4),ISND(50) SUMM=0.0D0
* This s * each c	subroutine will calculate the sum total error for latarun DSUM. The overall total is then returned as SUMM
	DO 10 I1=1,ISD DSUM=0.0D0 DELT=0.0D0 DO 20 I2=1,ISND(I1) T=TKS(I1,I2) GM0=FMS(I1,I2) VNM=VNS(I1,I2) TH=THS(I1,I2) ND=NDS(I1,I2) WSK=WSS(I1,I2) XB=XBS(I1,I2) VN2=VNS(I1,I2)
* TEFF * TEFF * DELT * DELT	1 time to form the previous measured fraction at this temp 2 time to form thepresent fraction at this temp 3 is the effective time increment 4 is the predicted reaction time for the present fraction
	TEFF2=NEWF(T,GM0,VN2,TH,ND,CD,WSK,XB) $L1=DLOG(TEFF2)$ $L2=DLOG(TIMS(I1,I2))$ $DSUM=DSUM+(L1-L2)**2$ $IF (IGO .EQ. 1) THEN$ $OPEN (UNIT=7,FILE='junk1.dat')$ $OPEN (UNIT=8,FILE='junk2.dat')$ $OPEN (UNIT=9,FILE='junk3.dat')$ $IF (ND .EQ. 46.7D0) IOUT=7$ $IF (ND .EQ. 51.975D0) IOUT=8$ $IF (ND .EQ. 86.00D0) IOUT=9$ $WRITE (IOUT,999) TIMS(I1,I2),TEFF2$

20 10 999	ENDIF CONTINUE SUMM=SUMM+DSUM CONTINUE FORMAT (' ',2F15.6) END
 * This fu	unction is the corrected theory presented in Chapter 3
 &	DOUBLE PRECISION FUNCTION NEWF (TK,GM0,PSI,THETA,ND,CD,WSS,XB) IMPLICIT DOUBLE PRECISION (A-H,L-Z),INTEGER (I-K) PARAMETER (R=8.314D0,RR=2540D0) DIMENSION CD(4) C1=CD(1) BETA=CD(2)*(1.0D0- CD(4)*XB) C2=CD(3) GSM=ND GNT= $3.636*(TK-273.15) -2540D0$ GNW= $3.636*(WSS-273.15) -2540D0$ GAMMA= C2*(GM0-GNT)/(RR*R*TK) LL =LOGS(PSI,GAMMA,BETA,THETA) E = DEXP(-C2/(R*TK) -C2*GM0/(RR*R*TK))) NEWF = C1*GSM*THETA*LL/E END
&	DOUBLE PRECISION FUNCTION LOGS(PSI,GAMMA,BETA,THETA) IMPLICIT DOUBLE PRECISION (A-H,L-Z) IMPLICIT INTEGER (I-K) A=DEXP(-GAMMA)/(1D0+BETA*THETA) C=CT(GAMMA,BETA,THETA)/CB(GAMMA,BETA,THETA) B= 1D0-A-C LOGS=(B/(BETA*THETA))*DLOG(1D0+BETA*THETA*PSI) (-A*DLOG(1D0-PSI) -(C/GAMMA)*(DEXP(-PSI*GAMMA)-1D0)) END
&z &z	DOUBLE PRECISION FUNCTION CT(GAMMA,BETA,THETA) IMPLICIT DOUBLE PRECISION (A-H,L-Z) IMPLICIT INTEGER (I-K) CT=1D0-DEXP(GAMMA/BETA)*(1D0-(1D0/BETA)) -DEXP((GAMMA/BETA) -GAMMA)*((1D0/(BETA*(1D0+BETA*THETA))) + (THETA/(1D0+BETA*THETA))) END
	DOUBLE PRECISION FUNCTION CB(GAMMA,BETA,THETA) IMPLICIT DOUBLE PRECISION (A-H,L-Z) IMPLICIT INTEGER (I-K) CB=(1D0-1D0/BETA)*(1D0+THETA-DEXP(GAMMA/BETA)) END

Program for Predicting Bainite Transformation Kinetics

	• •	•
* At present the program is set to give isothermal kinetics for	• •	·
* temperature in increments of 25 K above MS		
IMPLICIT DOUBLE PRECISION(A-H,L-Z),INTEGER(I-K) DIMENSION TC(1000),XT0(1000),GM0(1000),AE3(1000),X44(1000) DIMENSION CNS(4),THOLD(4) PARAMETER (S=0.69D-03) COMMON WS,GSM,CNS(4)	•••	•
* Open the output files	• •	•
open (unit=1,file='wa1.dat') open (unit=2,file='wa2.dat') open (unit=3,file='wa3.dat') open (unit=4,file='wa4.dat')		
GSM=50.0		
* Read the transformation start temperatures from the thermo file	• •	·
READ (5,*) IA READ (5,*) WS,BS,MS,XB		
* Open and read constants form the constants file OPEN (UNIT=7, file='theory/geff6/c') READ (7,*) (CNS(J1),J1=1,4)		
* Establish the temperatures to be considered		·
DO 5 IH=1,4 THOLD(IH)=INT(MS)+25.0D0*IH		
5 CONTINUE		
* Read the thermodynamic data for 200 - 700 degC DO 10 I1=1,999 READ (5,*,END=11) TC(I1),XT0(I1),GM0(I1),AE3(I1),X44(I1)		•
IO CONTINUE		
11 INUM=I1-1 IH=1 DO 20 I2=1,INUM		
	• •	·
Search for the desired temperatures IF (TC(I2) .EQ. THOLD(IH))THEN		•

TCC=TC(I2) XT=XT0(I2) GM=GM0(I2) X4=X44(I2) X3=AE3(I2)
* Ensure that we are below the bs temperature IF ((X4 .LT. XB) .OR. (XT .LT. XB)) GOTO 31
 * If trapping is accounted for, the relative thickness of the * ferrite plates and austenite films must be specified. 21 F=0.0D0
IOUT=IOUT+1 IF (IOUT .EQ. 5) IOUT=7
* Loop for taking the extent of transformation from 0 to theta DO 30 P=0.01D0,0.999D0,0.01D0 T=NEWF(P,TCC,TH,GM,XB,X3,XT,F)
 * At present output is set to the new theory. The previous theory * (Bhadeshia 1982) can be chosen if desired. * T2=OLDF(P,TCC,TH,GM)
WRITE (IOUT,999) P*TH,T,TCC 30 CONTINUE
31 IH=IH+1 ENDIF
20 CONTINUE
99 FORMAT(' ',2D15.5,F15.5) END
DOUBLE PRECISION FUNCTION NEWF(P,TC,THETA,FM,XB,X3,XT,F) IMPLICIT DOUBLE PRECISION (A-H,L-Z) IMPLICIT INTEGER(I-K) DIMENSION CNT(4) COMMON WS,GSM,CNT(4) PARAMETER (R=8.314D0,S=0.69D-03,RR=2540D0)
 * Establish the maximum extent of transformation allowable * either with trapping or wihtout.

THETA=(XB-XT)/((S+F*X3) - XT*(1.0D0-F)) BETA=CNT(2)*(1.0D0-CNT(4)*XB) C2=CNT(3) TK=TC+273.15d0 BT=1D0+BETA*THETA BTP=1D0+BETA*THETA*P B1B=1D0-1D0/BETA GNT=3.636D0*TC-2450.0D0 GAMMA= CNT(3)*(FM-GNT)/(RR*R*TK) DD=DEXP(GAMMA/BETA) A=DEXP(-GAMMA)/(BT) CT=1D0 - DD*(B1B +A*(1D0/BETA+THETA)) CB=B1B*(1D0+THETA -DD) C=CT/CB B=1-A-C IF (BTP .LT. 0.0) THEN WRITE (6,*) THETA PAUSE '1+BETA*THETA*PSI ; 1' ENDIF EE=DEXP(-C2/(R*TK) -C2*FM/(RR*R*TK)) LOGS=-A*DLOG(1D0-P) +(B/(BETA*THETA))*DLOG(BTP) & -(C/GAMMA)*(DEXP(-P*GAMMA)-1D0) NEWF=GSM*CNT(1)*THETA*LOGS/(EE) END	
* Subroutine to calculate the prediction made by Bhadehshia	
<pre>* for the reaction kinetics of bainite, old theory (1982) DOUBLE PRECISION FUNCTION OLDF(P,TC,THETA,FM) IMPLICIT DOUBLE PRECISION (A-H,L-Z) IMPLICIT INTEGER(I-K) DIMENSION CNT(4) PARAMETER (R=8.314D0,S=0.69D-03) COMMON WS,GSM,CNT(4) BBB = 199.999D0 C3 = 3.769D0 C2 = 29709.9D0 C1C=DEXP(9D0) WSS=WS+273.15D0 TK=TC+273.15D0 BT=1D0+BBB*THETA BTP=1D0+BBB*THETA</pre>	

```
B1B=1D0-1D0/BBB
    GNT=3.636D0*WS-2450.0D0
    GAMMA = 11D0*THETA*FM/(R*TK)
    DD=DEXP(GAMMA/BBB)
    A=DEXP(-GAMMA)/(BT)
    CT=1D0 - DD*(B1B + A*(1D0/BBB+THETA))
    CB=B1B*(1D0+THETA -DD)
    C = CT/CB
    B=1D0-A-C
    IF (BTP .LT. 0.0) THEN
       WRITE (6,*) THETA
       PAUSE '1+BBB*THETA*PSI ; 1'
    ENDIF
    LOGS = -A * DLOG(1D0 - P) + (B/(BBB * THETA)) * DLOG(BTP)
   & -(C/GAMMA)*(DEXP(-P*GAMMA)-1D0)
    EE = DEXP(C2*(WS-TC)/(R*TK*WSS) + (C3/R)*((FM/TK) - (GNT/WSS)))
    OLDF=C1C*THETA*EE*LOGS
    END
```

A Model for Acicular Ferrite Transformation Kinetics During Continuous Cooling

 * This program is written to run on a Sun Workstation * In its present form it will use the constants determined for * Harry's bainite kinetics data 	•
PROGRAM MAIN IMPLICIT DOUBLE PRECISION (A-H,L-Z) IMPLICIT INTEGER (I-K) CHARACTER*71 IFILE DIMENSION TC(2000),XT0(2000),FM(2000),X44(2000), & WEIGH(4),CO(8),AT(8),AR(8) COMMON WS,GSM,C1,LAM1,C2,LAM2 MAX=0.0D0 MSS=0.0	•
* Open constants file and read OPEN (UNIT=1,FILE='theory/geff6/c') READ (1,*) C1,LAM1,C2,LAM2	•
* Read alloy file name and open the file READ (5,*) IFILE OPEN (UNIT=4,FILE=IFILE)	•
OPEN (UNIT=7,FILE='theory/geff6/num') OPEN (UNIT=8,FILE='theory/geff6/iweight') OPEN (UNIT=9,FILE='temp.dat')	•
READ (8,*) IWEIGHT	•
 * Read in the data concerning inclusion content, and composition CALL DATAREAD(CO,AR,ALO,MNO) * Read in thermodynamic data for the alloy considered CALL THREAD(WS,BS,MS,XBAR,TC,XT0,FM,X44,J1) 	•
WEIGH(1)=ALO/121.0D0 WEIGH(2)=MNO/116.0d0 WEIGH(3)=((ALO/3.0D0)+MNO)/156.33D0 WEIGH(4)=1.0d0	·
 * At present the program is set up to vary the nucleation site * density parameter. The best value from output for all welding * alloys is the selected for optimim results. For this purpose * the grain size dependent variable GSM is varied. For the case * transformation to bainite set GR=1.0, GSM=grain size (microns) 	

```
* and set IWEIGHT=4.
DO 919 GR=1.91,3.0,0.05
        GSM=1.0d0/(WEIGH(IWEIGHT)*GR)
 I3 = 0
        IC=0
        TOT=0
        TSTEP=0
        MAX=0
        DO 40 I3=1,J1
     * Establishment of the continuous curve as a series of isothermal
* hold
* IF IPROF equals some number other than 0, a linear cooling rate
* employed. The desired cooling rate MUST BE SPECIFIED.
IPROF=0
           IF (IPROF .EQ. 0 ) THEN
              TSTEP = TFUN(TC(I3+1)) - TFUN(TC(I3))
              IF (I3 .EQ. 1) THEN
                 TOT = TFUN(TC(I3))
              ELSE
                 TOT=TOT+TSTEP
              ENDIF
           ELSE
              CR=15.0D0
              TSTEP = TLFUN(TC(I3+1), CR) - TLFUN(TC(I3), CR)
              IF (I3 .EQ. 1) THEN
                 TOT = TLFUN(TC(I3), CR)
              ELSE
                 TOT=TOT+TSTEP
              ENDIF
           ENDIF
       * Calculation of the volume fraction of ferrite formed at the end
* of the first isothermal hold. Then at subsequent temperatures the
* effective time for formation of the existing amount of ferrite is
* calculated, then growth is allowed for the duration of the current
* isothermal hold.
             IF ((XT0(I3).GT. XBAR).AND. (X44(I3).GT. XBAR)) THEN
              IF (TC(I3) .GT. (MS+1.0d0)) THEN
                 IC=IC+1
                 THETA = (XT0(I3)-XBAR)/(XT0(I3)-S)
                 IF (IC .GT. 1) THEN
                    P=V/THETA
                   TIME=NEWF(P,TC(I3),THETA,FM(I3),XBAR)+TSTEP
                 ELSE
```

	TIME=TSTEP
	ENDIF
	CALL PROOT(TC(I3),XT0(I3),FM(I3),X44(I3),P,TIME,
&	THETA, XBAR)
	TR=TC(I3)
	V=P*THETA
	IF (V.GT. MAX) THEN
	MAX=P*THETA
	ENDIF
	ELSE
	GOTO 918
	ENDIF
	ENDIF
40	CONTINUE
918	WRITE (6,928) MAX,GR
928	FORMAT (' ' 2F13.6,2D15.5)
	ICOUNT=ICOUNT+1
919	CONTINUE
	WRITE (7,*) ICOUNT
17	END

	DOUBLE PRECISION FUNCTION TFUN(T) IMPLICIT DOUBLE PRECISION (A-H,K-Z)
* Contin * (Greto) * Present	uous cooling curve expression for arc weld ft, Bhadeshia & Svensson, t parameters are set to submerged are values.
	CURR=500.0D0 V=29.0D0 S=0.92D-02 EFF=0.95 TINIT=900.0D0 TI=200.0D0 C1=0.4359D+04 C2=0.151D+01 TFUN=CURR*V*EFF*((TINIT-TI)**(1.0D0-C2)- (T, TI)**(1.0D0, C2))/(C1*S*(1.0D0, C2))
82	(1-11)**(1.0D0-C2))/(C1*5*(1.0D0-C2)) END

SUBROUTINE PROOT(TC,XT0,FM,X44,P,TIME,THETA,XB) IMPLICIT DOUBLE PRECISION (A-H,L-Z)

* Subroutine to find the normalised volume fraction that satisfies * the kinetics equation for a given reaction time. IMPLICIT INTEGER (I-K) IC=0P1=0.1D-08 P3=0.9999 1 P2=0.5D0*(P1+P3)IC=IC+1IF (IC .GT. 50) GOTO 11 IF(DABS(TROOT(P2,TC,THETA,FM,TIME,XB)) .LT. 0.01d0) GOTO 11 IF (TROOT(P2,TC,THETA,FM,TIME,XB) *TROOT(P1,TC,THETA,FM,TIME,XB) .LT. 0.00) THEN & P3=P2GOTO 1 ELSE P1=P2GOTO 1 ENDIF

11 P=P2 END

DOUBLE PRECISION FUNCTION NEWF (PSI,TCC,THETA,GM0,XB) IMPLICIT DOUBLE PRECISION (A-H,L-Z) IMPLICIT INTEGER (I-K) COMMON WS,GSM,C1,LAM1,C2,LAM2 PARAMETER (R=8.314D0,RR=2540D0) WSS=WS+273.15D0 T=TCC+273.15D0 GNT = 3.636 * (T - 273.15) - 2540D0GNW = 3.636 * (WSS - 273.15) - 2540D0GAMMA = C2*(GM0-GNT)/(R*RR*T)BETA = LAM1*(1.0d0 - LAM2*XB)LL =LOGS(PSI,GAMMA,BETA,THETA) E = DEXP(-C2/(R*T) - C2*GM0/(RR*R*T))NEWF = C1*GSM*THETA*LL/EEND

DOUBLE PRECISION FUNCTION TROOT(PSI,TC,THETA,GM0,TIME,XB) IMPLICIT DOUBLE PRECISION (A-H,L-Z) IMPLICIT INTEGER (I-K)

 * Function representing the reaction time to form a normalised * volume fraction PSI at tempreature TC. 	•
COMMON WS,GSM,C1,LAM1,C2,LAM2 PARAMETER (R=8.314D0,RR=2540D0) T=TC+273.15D0 * WSS=WS+273.15D0 GNT= 3.636*(T-273.15) -2540D0 * GNW= $3.636*(WSS-273.15) -2540D0GAMMA= C2*(GM0-GNT)/(R*RR*T)BETA= LAM1*(1.0D0-LAM2*XB)LL =LOGS(PSI,GAMMA,BETA,THETA)E = DEXP(-C2/(R*T) -C2*GM0/(RR*R*T))TROOT=TIME-C1*GSM*THETA*LL/EEND$	-
DOUBLE PRECISION FUNCTION LOGS(PSI,GAMMA,BETA,THETA) IMPLICIT DOUBLE PRECISION (A-H,L-Z) IMPLICIT INTEGER (I-K)	
 * Function representing the log and exponential terms involving * PSI in the kinetics equation. 	•
A=DEXP(-GAMMA)/(1D0+BETA*THETA) C=CT(GAMMA,BETA,THETA)/CB(GAMMA,BETA,THETA) B= 1D0-A-C LOGS=(-A*DLOG(1D0-PSI) & +(B/(BETA*THETA))*DLOG(1D0+BETA*THETA*PSI) & -(C/GAMMA)*(DEXP(-PSI*GAMMA)-1D0)) END	•
SUBROUTINE DATAREAD(COO,ARR,ALOO,MNOO) IMPLICIT DOUBLE PRECISION (A-H,L-Z),INTEGER(I-K) DIMENSION COO(8),ARR(8)	
READ (5,*) TI,AL,O	
* Read the alumina and magnesia content READ (5,*) ALOO,MNOO	•

* Read allow composition form the thermodynamics file	•
READ (4,*)	
READ $(4,*)$ (COO(I1I),I1I=1,7)	
COO(8) = 1D2 - ADD(COO, 7)	
	•
* Input relative atomic weights	
ARR(1) = 12.00	
ARR(2) = 28.086	
ARR(3) = 54.9	
ARR(4) = 58.71	
ARR(5) = 95.94	
ARR(6) = 51.99	
ARR(7) = 14.94	
ARR(8) = 55.847	
END	•

SUBROUTINE THREAD(WS,BS,MS,XBAR,T1,X1,F1,X4,J1) IMPLICIT DOUBLE PRECISION (A-H,L-Z), INTEGER(I-K) DIMENSION TTC(2000), TXT0(2000), TFM(2000), BLAH, TX44(2000) DIMENSION T1(2000),X1(2000),F1(2000),X4(2000) * First two line of data have already been read * Next line contains start temperatures and the mean carbon * mole fraction READ (4,*) WS,BS,MS,XBAR * Read thermodynamic quantities: * Temp, XT0, Driving Force (GM), XAE3 (not used), XN0 DO 10 I1=1,2000 READ (4,*,END=11) TTC(I1),TXT0(I1),TFM(I1),BLAH,TX44(I1) 10 CONTINUE J1=I1-1 11 * Reverse the order so that temperature decreases with array no. DO 20 I2=1,J1 T1(I2) = TTC(I1-I2)X1(I2) = TXT0(I1-I2)F1(I2) = TFM(I1-I2)X4(I2) = TX44(I1-I2)20CONTINUE . . . END

* CT is the numerator of the constant C (from separation of * the differential equation into partial fractions (Bhadeshia * 1982). CB is the denominator of the same constant. DOUBLE PRECISION FUNCTION CT(GAMMA, BETA, THETA) IMPLICIT DOUBLE PRECISION (A-H,L-Z) IMPLICIT INTEGER (I-K) CT=1D0-DEXP(GAMMA/BETA)*(1D0-(1D0/BETA)) & -DEXP((GAMMA/BETA) -GAMMA) *((1D0/(BETA*(1D0+BETA*THETA)))) & & + (THETA/(1D0+BETA*THETA))) END DOUBLE PRECISION FUNCTION CB(GAMMA, BETA, THETA) IMPLICIT DOUBLE PRECISION (A-H,L-Z) IMPLICIT INTEGER (I-K) CB=(1D0-1D0/BETA)*(1D0+THETA-DEXP(GAMMA/BETA)) END * Included so that linear cooling curve can be chosen DOUBLE PRECISION FUNCTION TLFUN(CTEMP,CR) IMPLICIT DOUBLE PRECISION (A-H,L-Z), INTEGER(I-K) TLFUN=(900.0-CTEMP)/CR END * Function to add the elements within an array up to a * specified number DOUBLE PRECISION FUNCTION ADD(X,I) IMPLICIT DOUBLE PRECISION (A-H,L-Z), INTEGER (I-K) DIMENSION X(8) A=0.DO 10 I1=1,I A = A + X(I1)10CONTINUE ADD=AEND

A Model for the Hardness of High Strength Weld Microstructures IMPLICIT DOUBLE PRECISION (A-H,L-Z), INTEGER(I-K) INTEGER IARR, IADD, IALL PARAMETER (IARR=8, IADD=IARR-1, IALL=1) COMMON IAR, IAL * IARR=ARRAY SIZE, IALL=NUMBER OF ALLOYS ANALYSED DIMENSION C(IARR, IALL), AT(IARR, IALL), AR(IARR) DIMENSION ATP(IARR, IALL), CP(IARR, IALL), HTOT(IALL), V(IALL) WRITE (6,*) 'REMEMBER THAT NITROGEN MUST BE IN THE DATASET' IAR=IARR IAL=IALL DO 10 I1=1,IALL READ (5,*) (C(J1,I1),J1=1,IADD),V(I1),HTOT(I1) C(IARR,I1) = 100.0-ADD(C,I1,IADD)10CONTINUE AR(1) = 12.00AR(2) = 28.086AR(3) = 54.9AR(4) = 58.71AR(5) = 95.94AR(6) = 51.99AR(7) = 14.94AR(8) = 55.847MIN=1D10 K=353.70d0 * Decides whether to optimise or print out results 1 K = K + 1.0D0SUMM=0.0D0 DO 20 I2=1,IAL CALL ATFRAC(C,AT,AR,I2) STRSUB=DELSIG(AT,I2) STRNIT=NITROG(C,I2) STRENGTH=STRSUB+STRNIT CALL ENRICH(V,AT,ATP,I2) CALL WT(ATP,CP,AR,I2) STRM=3.0D0*MNH(C,I2) * Variable Separation for Phoenix analysis

&	YY= 3.0D0*HTOT(I2) - STRM*(1.0D0-V(I2)) - V(I2)*STRENGTH XX=V(I2)
* 20	PRED= V(I2)*(STRENGTH+K) +(1.0D0-V(I2))*STRM SUMM = SUMM+ (PRED-3.0D0*HTOT(I2))**2.0 WRITE (6,*) PRED/3d0, HTOT(I2) WRITE (6,*) XX,YY CONTINUE IF (SUMM .LT. MIN) THEN BEST=K MIN=SUMM ENDIF ICOUNT=ICOUNT+1 IF (ICOUNT .LT. 1000) GOTO 1 END
• • • • • • • • • • • • • • • • • • •	cal function to add elements in an array
	DOUBLE PRECISION FUNCTION ADD(X,I,IX) IMPLICIT DOUBLE PRECISION (A-H,L-Z),INTEGER (I-K) COMMON IARR,IALL DIMENSION X(IARR,IALL) A=0. DO 10 I1=1,IX A=A+X(I1,I) CONTINUE ADD=A
	END
* Subro	ATFRAC(CC,CAT,ARR,IAT) IMPLICIT DOUBLE PRECISION (A-H,L-Z),INTEGER(I-K) COMMON IARR,IALL PARAMETER (IAR=8,IAL=10) DIMENSION CC(IARR,IALL),COM(IAR,IAL),CAT(IARR,IALL) DIMENSION SUM(IAL),ARR(IARR) DO 10 J1=1,IARR COM(J1,IAT) = CC(J1,IAT)/ARR(J1)
10	CONTINUE SUM(IAT)=ADD(COM,IAT,IARR) DO 13 J2=1,IARR
13	CAT(J2,IAT)=COM(J2,IAT)/SUM(IAT) CONTINUE END

- * Calculates the strengthening contributions* of substitutional elements in iron

 & & &	DOUBLE PRECISION FUNCTION DELSIG(AT1,JD) IMPLICIT DOUBLE PRECISION (A-H,L-Z),INTEGER(I-K) COMMON IARR,IALL DIMENSION AT1(IARR,IALL) SFE=220. STOT= SFE + AT1(2,JD)*(5215.0D0) + AT1(3,JD)*3510.33D0 + AT1(4,JD)*3937.667D0 + AT1(6,JD)*93.967D0 DELSIG=STOT END	
• • • • • • • • • • • • • • • • • • •	ates the effect of carbon enrichment on austenite composition c fractions	
10	ENRICH (VE,ATE,APE,IE) IMPLICIT DOUBLE PRECISION (A-H,L-Z),INTEGER (I-K) COMMON IARR,IALL PARAMETER (IAR=8,IAL=10) DIMENSION ATE(IARR,IALL),APE(IAR,IAL) PARAMETER (S=0.69D-03) XGP = (ATE(1,IE) - VE*S)/(1.0D0-VE) APE(1,IE)=XGP DO 10 I1=2,8 APE(I1,IE)=ATE(I1,IE)*(1.0D0-XGP) CONTINUE END	
* Calculates the weight percentage from atomic fractions		
	WT(AW,CW,ARW,IW) IMPLICIT DOUBLE PRECISION (A-H,L-Z),INTEGER (I-K) COMMON IARR,IALL DIMENSION CW(IARR,IALL),AW(IARR,IALL),ARW(IARR,IALL) TOT=0.0 DO 10 I1=1,IARR TOT=TOT + AW(I1,IW)*ARW(I1,IW)	
10	CONTINUE DO 11 I2=1,IARR	
11	CW(I2,IW)=1.0D+02*(AW(I2,IW)*ARW(I2,IW)/TOT) CONTINUE END	

* Calculated the hardness of martensite for a given composition

```
DOUBLE PRECISION FUNCTION MNH(CM,IM)
     IMPLICIT DOUBLE PRECISION (A-H,L-Z), INTEGER(I-K)
     COMMON IARR, IALL
     DIMENSION CM(IARR, IALL), CF(6)
     CF(1) = 670.0D0
     CF(2) = -73.0D0
     CF(3) = 34.0D0
     CF(4) = 12.0D0
     CF(5) = -8.0D0
     CF(6) = 61.0D0
     MNH = CF(1) * DSQRT(CM(1,IM))
  \& + CF(2) * CM(2, IM)
  \& + CF(3) * CM(3, IM)
  \& + CF(4) * CM(4, IM)
  \& + CF(5) * CM(5, IM)
  \& + CF(6) * CM(6, IM) + 132.0d0
     END
* Calculates the effect of nitrogen on strength
DOUBLE PRECISION FUNCTION NITROG(CC, INIT)
     IMPLICIT DOUBLE PRECISION (A-H,L-Z), INTEGER(I-K)
     COMMON IARR, IALL
     DIMENSION CC(IARR, IALL)
     NIT = CC(7, INIT)
     NITROG=7.35D0 - 4400D0*NIT - 59400D0*(NIT**2)
     END
```

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