ACICULAR FERRITE AND BAINITE
IN
Fe-Cr-C WELD DEPOSITS

by
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To my mother
Smt. S. Rajalakshmi
PREFACE

This dissertation is submitted for the degree of Doctor of Philosophy at the University of Cambridge. It describes the work carried out under the supervision of Dr. H. K. D. H. Bhadeshia in the Department of Materials Science and Metallurgy, Cambridge, between October 1988 and September 1991. Except where appropriately referenced, this work is entirely original, and contains nothing which is the outcome of collaboration. No part of this dissertation has been, or is concurrently being, submitted for any other degree, diploma or any other qualification. It does not exceed 60,000 words in length.


Suresh Babu S.

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ABSTRACT

This project is a part of the continuing research to predict the evolution of microstructure and properties in steel welds.

It has been suggested that an increase in the Cr and Mo concentration in steel welds should lead to a corresponding increase in the fraction of acicular ferrite, which is a desirable microstructure. In fact, the acicular ferrite volume fraction goes through a maximum as the Cr and Mo concentrations are increased. It is found that this unexpected effect can be attributed to a transition from acicular ferrite to bainite. Factors controlling the transition from acicular ferrite to bainite have been investigated. It appears that the presence of allotriomorphs of ferrite at the austenite grain boundaries has the effect of suppressing the formation of bainitic sheaves. This, in turn allows the acicular ferrite plates to develop on intragranular nucleation sites. A theoretical analysis indicates that the bainitic transformation is prevented from developing at the allotriomorphic ferrite/austenite boundaries by the carbon concentration profile present in the austenite at the allotriomorphic ferrite/austenite interface.

The crystallography of the grain boundary allotriomorphic ferrite has been studied with the aim of estimating the fraction of ferrite-austenite interfaces capable of developing into plates of Widmanstätten ferrite. The direct measurement of austenite orientation was made possible by using steels containing relatively large concentrations of silicon, heat treated in two stages to enable the retention of a substantial volume fraction of austenite at room temperature. The fraction of allotriomorphs exhibiting a reproducible orientation relationship with austenite is found to be rather small, as a consequence of the higher mobility of more incoherent $\alpha - \gamma$ boundaries. Allotriomorphs showing an orientation relationship with both the adjacent austenite grains are found to be very rare. The tendency for the allotriomorph to adopt an orientation which optimizes its fit with respect to both austenite grains with which it is in contact is also found to be small. Microanalysis data and their theoretical interpretation confirm that the transition from equilibrium to para-equilibrium growth can not be predicted by the usual method based on an estimation of the solute diffusion distance in the austenite.

For successful transition from bainite to acicular ferrite, the allotriomorphic ferrite has to be inert, i.e., unable to develop into Widmanstätten ferrite or bainite sheaves. Detailed experiments are reported to verify that the allotriomorphic ferrite can be rendered inert by the build up of carbon in the austenite ahead of the allotriomorphic ferrite/austenite boundary. Controlled experiments, simulating the continuous cooling characteristics of welding, illustrated the importance of cooling conditions on acicular ferrite microstructure development. The temperature at which the maximum extent of transformation to acicular ferrite occurs is related to its plate size.
Acicular ferrite is considered to be identical in transformation mechanism to bainite, except that it nucleates intragranularly on inclusions, and hence develops into a morphologically different microstructure. The transformation causes displacements which, on a macroscopic scale, are characteristic of an invariant-plane strain with a large shear component. It is therefore expected that the transformation should be sensitive to an appropriate, externally applied stress. Results are presented which demonstrate quantitatively that large changes in the development of the microstructure are induced when acicular ferrite grows while the austenite is in compression. This is in spite of the fact that the applied stress used was below the austenite yield strength.

Cobalt (4.3 wt.%) was added to Fe-0.04C-2.25Cr-1Mo (wt.%) welds to stimulate the formation of allotriomorphic ferrite, and hence of acicular ferrite. No effect on allotriomorphic ferrite reaction kinetics was observed and hence no acicular ferrite formed in the welds. The reasons for this are unknown at this point and further work is needed.
Nomenclature and Abbreviations

\( a_\gamma^a \)  
Lattice parameter of unalloyed austenite

\( \bar{a}_\gamma \)  
Lattice parameter of alloyed austenite

\( \bar{a}_\alpha \)  
Lattice parameter of ferrite at ambient temperature

\( a_{Fe}^\alpha \)  
Lattice parameter of pure iron at ambient temperature

\( AE_3 \)  
Upper limiting temperature of the \( \alpha + \gamma \) phase field at equilibrium

\( AE_3' \)  
Upper limiting temperature of the \( \alpha + \gamma \) phase field at paraequilibrium

\( AE_1' \)  
Lower limiting temperature of the \( \alpha + \gamma \) phase field at paraequilibrium

AWS  
American Welding Society

\( BS \)  
Bainitic transformation start temperature

\( C_i \)  
Coefficient relating the effect of the concentration of element \( i \) on the lattice parameter of austenite

CCT  
Continuous Cooling Transformation Diagram

\( D \)  
Weighted average diffusivity of carbon in austenite

\( e_c \)  
Expansion in lattice parameter due to dissolved carbon

\( e_\alpha \)  
Linear thermal expansion coefficient of ferrite

\( e_\gamma \)  
Linear thermal expansion coefficient of austenite

KS  
Kurdjumov-Sachs orientation relationship

\( k_e \)  
Equilibrium partition coefficient

\( k_p \)  
Non-equilibrium partition coefficient

\( MS \)  
Martensitic transformation start temperature

\( MS_{Si,Mn,...} \)  
Mole fractions of alloying elements in the alloy

NW  
Nishiyama-Wasserman orientation relationship

\( q \)  
Half thickness of allotriomorphic ferrite

\( T_0 \)  
Temperature at which ferrite and austenite of identical composition have the same free energy

\( T_0' \)  
Temperature at which ferrite and austenite of identical composition have the same free energy, taking into account the strain energy of the ferrite

\( T_i \)  
Isothermal heat treatment temperature

\( T_C \)  
Temperature at which the upper and lower ‘C’ curves of the TTT diagram intersect

\( T_\alpha \)  
Allotriomorphic ferrite transformation temperature

\( T_a \)  
Intermediate annealing treatment temperature

\( T_b \)  
Transformation temperature below \( B_s \)

\( T_h \)  
Highest temperature at which allotriomorphic ferrite growth starts
$T_l$  Temperature at which allotriomorph ferrite growth stops

TTT  Time-Temperature-Transformation

$T_S$  Temperature at which allotriomorph ferrite formation begins during the cooling of austenite

$T_1$  First isothermal heat treatment temperature

$T_2$  Second isothermal heat treatment temperature

$T_\gamma$  Austenitising temperature

$W_s$  Widmanstätten ferrite transformation start temperature

$\bar{x}_c$  Average carbon concentration of the alloy

$x_c^{\alpha\gamma}$  Paraequilibrium $\alpha/\gamma$ interface carbon concentration in ferrite

$x_\gamma^{\alpha}$  Paraequilibrium $\alpha/\gamma$ interface carbon concentration in austenite

$x_{T_0}$  Carbon concentration in austenite, as given by the $T_0$ curve

$x_{T_0}'$  Carbon concentration in austenite, as given by the $T_0'$ curve

$V_a$  Volume fraction of acicular ferrite

$V_\alpha$  Volume fraction of allotriomorph ferrite

$V_W$  Volume fraction of Widmanstätten ferrite

$V_m$  Volume fraction of microphases

$\alpha$  Allotriomorph ferrite

$\alpha_1$  One dimensional parabolic thickening rate constant for paraequilibrium growth of ferrite

$\alpha_a$  Acicular ferrite

$\alpha_b$  Bainitic ferrite

$\alpha_W$  Widmanstätten ferrite

$\gamma$  Austenite

$\delta$  delta ferrite

$\Delta G_{\text{max}}$  Maximum driving force for nucleation of ferrite from austenite

$\Delta G^{\gamma\rightarrow\alpha+\gamma'}$  Free energy change for austenite $\rightarrow$ austenite + ferrite

$\Delta G^{\gamma\rightarrow\alpha}$  Free energy change for austenite $\rightarrow$ ferrite with supersaturation

$\Delta t_{850-T_1}$  Time required to cool the sample from 850 °C to $T_1$, in seconds

$\tau_s$  Time taken to establish a steady state nucleation rate
Chapter 1

Introduction

Modern manufacturing methods aim at optimising design and quality, hopefully without extra cost. This necessitates stringent selection of the manufacturing process variables for specific requirements, without much pre-production work. Models can help in predicting the response for the known set of variables.

Recently, Kirkaldy (1991) stressed the importance of modelling the thermomechanical behaviour of steels (Fig. 1.1). The approach is to predict the phase diagrams, kinetics of phase transformations and application of the same to transient heat and load conditions. Most of the manufacturing process like forging, rolling, casting and welding involve one or more of the variables mentioned in Fig. 1.1. The present research project pertains to the development of microstructure in steel welds. The theory discussed and developed can be of general use in the physical metallurgy of steels.

Welding has been applied in all critical fields like power plant, nuclear constructions, pipe lines, offshore structures and ship building. A fundamental understanding of the problems associated with welding has led to the development of welding procedures and specifications to a highly sophisticated level (Baker, 1975). These standard practices, mainly empirical codes, were developed by studying the properties of steel welds in conjunction with microstructure. In spite of this understanding and experience, pre-production approval tests are almost a standard requirement for any welded joint. This makes the selection of welding processes and variables itself, an expensive endeavour. A theoretical approach based on physical principles can therefore be beneficial.

The model developed by Bhadeshia et al., (1985a) is a first step towards this approach; it successfully predicts the primary weld metal microstructure. The model also has been applied towards theoretical design of alloys for high strength weld metals, in a systematic new methodology. The present research project was initiated to explain certain anomalies observed in prediction of microstructure in Fe-Cr-Mo-C welds. The purpose here is to introduce, welding terminology, aspects of steel welding metallurgy and chromium-molybdenum steels. The basis of the research described in the rest of this thesis, is presented at the end of this chapter.

1.1 Fusion Welding

Fusion welding is a permanent joining method, in which parts are joined together by melting.

1.1.1 Welding Processes

A widely used welding process is manual metal arc welding (MMAW or SMAW). An electric
arc is struck between a consumable metal rod, coated with mineral and metallic particles, and the joint as shown in Fig. 1.2. The movement of the electrode over the joint area is carried out by a qualified welder. This type of welding is the most flexible and versatile technique. Another common process is gas metal arc welding (GMAW or MIG), in which a continuously fed solid wire replaces the electrode of SMAW and the shielding is achieved by a flow of inert gas around the arc. In case of steel welding CO₂ gas is used. The productivity for GMAW is higher than SMAW. For thick plate structures, of the kind usually encountered in power plant steam headers and reactor vessels, submerged arc welding (SAW) or electroslag welding (ESW) is used. Both the processes use a molten slag as the main shielding medium to isolate the hot metal from the environment.

The properties of the weld depend on the microstructure, which relies on transient cooling conditions and restraints on the welds. Heat input given to the joint controls the cooling conditions. The heat input (Q) is determined by the welding voltage (V), the welding current (I) and the speed of welding (v_s), which is represented as:

\[ Q = \frac{\eta VI}{v_s} \]  

(1.1)

where \( \eta \) is the heat transfer efficiency (\(< 1.0\)), which depends on the welding process. Extensive work has been carried out to enable the prediction of the cooling conditions for a given weld geometry, using analytical equations, extensive numerical methods like finite difference and finite element methods (Rosenthal, 1941, Christensen et al., 1965, Gray and Spence, 1982, Easterling, 1983).

1.1.2 Welding Metallurgy

There are two distinct regions of the joint which are of importance, namely, the weld metal (WM) and the heat affected zone (HAZ) as shown in Fig. 1.3.

**Weld Metal:**

This is the filled-in portion of the joint gap, which actually bonds the base-plates. The weld metal exhibits a columnar solidification microstructure similar to 'as cast' structures. The evolution of this columnar microstructure is often described as "epitaxial growth" (Easterling, 1983). The solidifying grain is a continuation of a base plate grain at the fusion boundary. The activation energy for solidification is thus zero. The reviews by Savage (1980) and Davies and Garland (1975) discuss the effect of welding variables on the weld metal solidification structure. The columnar grain size and shape can be changed by altering the weld pool shape. The inoculation of the weld pool, oscillation of the welding arc by mechanical or electromagnetic techniques, welding current and voltage modulation, ultrasonic vibration and forced surface nucleation all influence the solidification microstructure (Kou, 1987, Davies and Garland, 1975).
Heat Affected Zone:

The heat affected zone, is the region in the base plate whose microstructure is changed as the temperature rises during welding, but remains below the solidus temperature. Any microstructural change depends on the alloy and its starting condition. On moving from the fusion line towards the original base metal structure, distinct regions can be observed within the HAZ, depending upon the peak temperature \( T_p \) to which it is heated (Fig. 1.3). These include the coarse austenite grain region, heated to 1300–1100 °C, fine austenite grain regions (1100–900 °C), partially austenitised region (900–700 °C) and tempered region (500–700 °C) (Reed, 1990, Srinivasan, 1985). The temperature ranges are approximate and it should be stressed that the classification of regions using the equilibrium phase diagrams are not appropriate, instead kinetic considerations have to be considered. The heat affected zone, especially in the coarse austenite grain region, may transform to hard constituents like martensite, which can degrade the weldment properties by embrittlement. The main difference between the HAZ and weld metal lies in the austenite grain structure and the large inclusion content of the latter. Details of the differences in transformation behaviour are discussed later.

1.2 Austenite to Ferrite Transformation

A better understanding can be gained when all the decomposition reactions of austenite are viewed together. There is ample evidence that the different forms of ferrite can be categorised into those which are displacive and the others which involve a reconstructive transformation mechanism.

1.2.1 Reconstructive Transformations

Reconstructive transformation involves a change in crystal structure and with possible redistribution of solute contents between parent and product phase. In this mode, atoms make random thermally activated random jump across the transformation interface. All elements including solvent atoms (Fe) diffuse during transformation in a way which minimises the strain energy.

1.2.2 Displacive Transformations

During displacive transformations, the atoms move less than an interatomic distance and retain their relative relationships with their neighbours. The transformation process per se is equivalent to the deformation of the parent crystal lattice (austenite) to the product crystal lattice (ferrite), an invariant plane strain shape deformation with a large shear component. No iron or substitutional alloying element diffusion takes place.

The structural change during displacive and reconstructive transformations differ and is explained schematically in Fig. 1.4. The different ferrite products that occur in welds as variations
of these two mechanisms of transformations are as as follows;

- Allotriomorphic ferrite
- Widmanstätten ferrite
- Bainite
- Acicular ferrite
- Martensite

The mechanisms of transformation for the above phases are grouped as shown in Fig. 1.5. The martensite and austenite, which usually form in welds as aggregates, are known as "microphases". The volume fraction of these is often very low in the case of low alloy steel weld deposits. The microstructure classification listed above is slightly different from the one proposed by the Welding Institute (Pargeter, 1983). The terminology by the Welding Institute considers Widmanstätten ferrite and bainitic ferrite as a single constituent. Each phase is now discussed in detail.

1.2.3 Allotriomorphic ferrite formation:

The allotriomorphic ferrite, (often called proeutectoid ferrite, grain boundary ferrite or polygonal ferrite), is the first phase to transform from austenite, on cooling. The term "allotriomorphic" means that the phase is crystalline in internal structure, but not in outward form (Christian, 1975). The allotriomorphic ferrite invariably nucleates along γ/γ boundaries and grows by a reconstructive transformation mechanism. The growth is not restricted by austenite grain boundaries.

The kinetics of grain boundary allotriomorphs has been studied extensively by many researchers (see review by Bhadeshia, 1985). The growth of allotriomorphic ferrite in Fe-C steel involves the partitioning of carbon into austenite and in most cases is limited by the diffusion of carbon in the austenite ahead of the interface. The diffusion-controlled growth of ferrite in Fe-C-X (where X represents a substitutional solute) steels is complicated by the fact that both interstitial and substitutional diffusion occurs during transformation. The respective diffusion coefficients differ substantially. In addition to this, the assumption of local equilibrium at the interface leads to a variety of possible growth modes (Hillert, 1951 and Coates, 1973c). To match the interstitial and substitutional fluxes and arrive at a unique α/γ interface velocity is only possible by varying the the concentration gradients. For example, in the Fe-C-Mn system, the transformation involves diffusion of manganese and carbon (partitioning of both C and Mn into austenite). This leads concentration profiles ahead of the moving interface as shown schematically in Fig. 1.6a. The interface compositions are under the local equilibrium assumption related by a tie-line for Fe-C-Mn phase diagram at that temperature. The conservation of mass at planar interface moving with a interface velocity "ν", in the direction Z (normal to the
interface plane) requires that in the first approximation;

\[
(x_{c}^\gamma - x_{c}^\alpha)\nu = -D_{11} \nabla x_{c}
\]  \hspace{1cm} (1.2)

\[
(x_{Mn}^\gamma - x_{Mn}^\alpha)\nu = -D_{22} \nabla x_{Mn}
\]  \hspace{1cm} (1.3)

where \(x_{c}\) and \(x_{Mn}\) represent concentrations of C and Mn and the gradients (\(\nabla x_{Mn}, \nabla x_{c}\)) are evaluated at the position of the interface. \(x_{c,Mn}^\alpha, x_{c,Mn}^\gamma\) are the compositions of the austenite and ferrite at the interface. \(D_{11}\) and \(D_{22}\) represent the diffusivities of C and Mn, as \(D_{11} \gg D_{22}\), these equations can not be in general be simultaneously satisfied, by a tie-line passing through \(x_{c}\) and \(x_{Mn}\). However, one possibility is to by select a tie line such that \(x_{c}^\gamma \simeq x_{c}\) (see Fig. 1.6b), so that flux of carbon is reduced to a rate consistent with diffusion of Mn. Ferrite growing by this mechanism is said to grow by "Partitioning Local Equilibrium" (PLE) mechanism, with long range diffusion of Mn in \(\gamma\).

An alternate choice of tie line would be to allow \(x_{Mn}^\gamma \simeq x_{Mn}\), in which case the Mn gradient is increased, thus allowing it keep pace with C, satisfying the mass conservation (see Fig. 1.6c). This mode of ferrite transformation is said to occur by a "Negligible Partitioning, Local Equilibrium" (NPLE) mechanism. Both the transformation mechanisms involve local equilibrium because the composition of the interface are determined by a tie line of the phase diagram.

Kinetic factors often prevent transformations from occurring under equilibrium conditions. An example case is a phase change which so rapid that one or more of the components can not redistribute among the phases in the time scale of the experiment (Cahn, 1980). In steels the diffusivities of interstitial and substitutional alloying element are very different. It is then possible to imagine a condition where the substitutional alloying element diffusion is so sluggish during \(\gamma \rightarrow \alpha\) transformation and substitutional alloying elements may not partition, even though carbon may be allowed to partition (Hillert, 1951, Rudberg, 1952 and Aaronson et al., 1966b). This constrained equilibrium between \(\alpha\) and \(\gamma\), where both phases have same substitutional to iron atom ratio, and yet the carbon achieves its equilibrium with both phases, is called "Paraequilibrium". The interface compositions are then given by the tie line to paraequilibrium phase diagram.

Because of the high cooling rates involved, the growth of allotriomorphic ferrite in welds can be assumed to occur by paraequilibrium transformation in which case it is is controlled by the diffusion of carbon in the austenite ahead of the interface. The half-thickness of an allotriomorph at an austenite grain boundary for a particular time at a transformation temperature is given by following equation for one-dimensional thickening.

\[
\]
\[ q = \alpha_1 t^{0.5} \]  

(1.4)

where

\( \alpha_1 \) is the one dimensional parabolic thickening rate constant

\( t \) is the time after the initiation of growth.

\( q \) is the half thickness of ferrite

The parabolic thickening rate is derived by solving the equation:

\[ 2(D/\pi)^{0.5} \left( \frac{x_e^{\gamma} - \bar{x}_e}{x_e^{\gamma} - x_e^{\gamma}} \right) = \alpha_1 \exp \left\{ \frac{\alpha_1^2}{4D} e rf_c \left( \frac{\alpha_1}{2D^{1/2}} \right) \right\} \]  

(1.5)

where

\( x_e^{\gamma} \) is the paraequilibrium carbon in austenite,

\( x_e^{\gamma} \) is the paraequilibrium carbon in ferrite,

\( \bar{x}_e \) is the average carbon concentration in the alloy,

\( D \) is a weighted average diffusivity of carbon in austenite given by Trivedi and Pound (1967).

\[ D = \int_{x_e^{\gamma}}^{x_e} \frac{D\{X\}}{\bar{x}_e - x_e^{\gamma}} \, dx \]  

(1.6)

where \( D\{X\} \) is calculated based on the method due to Siller and McElhanan (1969,1970) and Bhadeshia (1981b). The method takes into account the concentration dependence of the diffusivity of carbon in austenite. The calculation thus requires a knowledge of the phase diagram; the method for estimating such diagrams has been already developed by Bhadeshia and Edmonds (1980). The application of these ideas to continuous cooling conditions of weld are presented in the next section.

1.2.4 Widmanstätten ferrite formation

Widmanstätten ferrite forms as thin wedge shape plates nucleated from austenite grain boundaries. It always has a KS/NW type crystallographic orientation relationship with the austenite. Secondary Widmanstätten ferrite develops from the grain boundary allotriomorphic ferrite. It is believed that Widmanstätten ferrite grows by a displacive mechanism because there is an invariant-plane strain (IPS) shape change accompanying its growth. The strain energy due to the shape change is reduced (to about 50 J mol\(^{-1}\)) by the coupled growth of mutually accommodating variants. The rate is, however, controlled by the diffusion of carbon in austenite. Widmanstätten ferrite can occur as packets of plates. The thickening of these plates will be stifled by the diffusion fields of nearby plates (often called "soft impingement"). The lengthening rate \( G \) of Widmanstätten ferrite can be estimated using Trivedi's (1970) theory for the diffusion
controlled growth of parabolic cylinders. Because of its shape, and unlike allotriomorphic ferrite, Widmanstätten ferrite grows at a constant rate as long as soft impingement does not occur.

1.2.5 Bainite formation:

Bainite is often found in the weld metals having high alloy contents and occurs as a non-lamellar mixture of ferrite with or without carbides. The ferrite is in the form of clusters of thin platelets, called sub-units. Bainitic transformation leads to an IPS shape change and occurs without substitutional alloying element partition. The mechanism appears to be displacive (Bhadeshia and Edmonds, 1980). The sheaf grows by the repeated nucleation and growth of new sub-units. The initial nucleation event takes place at the prior austenite grain boundaries and subsequently, sub-units nucleate and grow from the tips of the previous sub-units (Christian and Edmonds, 1984, Bhadeshia and Christian, 1990).

The formation of bainitic ferrite leads to an increase in carbon concentration of the remaining austenite. It is believed that the bainitic ferrite sub-unit forms without any carbon compositional change, but after the transformation event carbon then diffuses rapidly into the austenite. There are two morphological bainitic ferrites observed in steel. Upper bainite is obtained if the time taken for the carbon diffusion process is small when compared with that required for the precipitation of carbides in the bainitic ferrite. Otherwise the transformation product is conventionally classified as lower bainite, with carbides being present inside the bainitic ferrite. The morphology of individual plates of bainite is determined by the need to minimise the strain energy owing to the IPS shape change associated with the displacive transformation. The bainitic transformation also exhibits characteristic IPS surface relief effect. The elastically accommodated strain energy is estimated to be around 400 J mole⁻¹.

Bainite forms below the $T_o$ temperature where the austenite and bainitic ferrite of the same chemical composition have equal free energy. This makes it thermodynamically possible for the transformation to be diffusionless. The diffusion of the carbon from the ferrite into the austenite constantly enriches austenite. The time scale of this process is of the order of fraction of a second. This makes it impossible to determine directly the concentration of carbon in the ferrite during its growth. There is, however, an indirect method of assessing the conditions that exist during transformation. If the carbon concentration of the austenite ($x_a$) exceeds that given by the $T_o$ curve, the diffusionless transformation stops. It has been verified using many different experimental techniques (Bhadeshia and Christian, 1990) that the growth of bainitic ferrite stops at the phase boundary where $x_a \simeq x_{T'_o}$. The $T'_o$ considers the strain energy of ferrite also (see Fig. 1.7).

The lengthening of bainitic platelets occurs at a rate much faster than would be expected from growth being controlled by diffusion of carbon in the austenite ahead of the interface.
Direct observation of the interface using the atom probe technique have demonstrated that substitutional solute atoms such as manganese, silicon, chromium, nickel and molybdenum do not partition between the phases during the bainitic transformation, nor do they segregate to the transformation interface (Bhadeshia and Waugh, 1982).

1.2.6 Acicular ferrite formation:

There has been extensive research in the field of acicular ferrite development in welds with reference to effects of alloy compositions, cooling rate and other welding variables and the effect of this microstructure on properties (see reviews by Abson and Pargeter, 1986, Farrar and Harrison, 1987 and Grong and Matlock, 1986 and Ricks et al., 1981 & 1982). The acicular ferrite is believed to give an optimum strength and toughness due to its fine grains and also the interlocking nature, often referred to as a “basket weave structure” (Liu and Olson, 1986). It is generally recognised that acicular ferrite has, in three dimensions, the shape of thin lenticular plate. The aspect ratio in a random section is about 0.1. The plates also contain a high dislocation density (Yang and Bhadeshia, 1990). The reviews by Grong and Matlock (1986) and Abson and Pargeter (1986), highlighted the mechanism of acicular ferrite formation and its effect on properties. There appears to be a strong dependence of the transformation on intragranular (within austenite matrix) inclusions. Some of the similarities between bainite and acicular ferrite can be summarised as follows:

1. There is no substitutional solute partitioning during the growth of either bainite or acicular ferrite (Strangwood and Bhadeshia, 1987a).

2. Both reactions stop when the austenite carbon concentration reaches a value where it becomes thermodynamically impossible to achieve diffusionless growth (Yang and Bhadeshia, 1987a; Strangwood and Bhadeshia, 1987a).

3. Acicular ferrite only forms below the bainite–start temperature (Ho et al., 1982).

4. There is a large and predictable hysteresis in the temperature at which austenite formation begins from a mixed microstructure of acicular ferrite and austenite, or bainite and austenite (Yang and Bhadeshia, 1987b,c, 1989b).

5. The removal of inclusions from a weld deposit, without changing any other feature, causes a change in the microstructure from acicular ferrite to bainite (Harrison and Farrar, 1981).

6. An increase in the number density of austenite grain surface nucleation sites (relative to intragranular sites) causes a transition from acicular ferrite to bainite (Yang and Bhadeshia, 1987a).

7. Like upper and lower bainite, it is possible to obtain upper and lower acicular ferrite. Plates of lower acicular ferrite, like lower bainite, contain fine precipitates of cementite in a single orientation (Sugden and Bhadeshia, 1989b).
8. At free surfaces, both acicular ferrite and bainite cause displacements which are characterised as invariant-plane strains with large shear components. Consequently, the growth of a plate of acicular ferrite or bainite is confined to a single austenite grain (i.e., it is hindered by a grain boundary) since the coordinated movement of atoms implied by the shape change cannot in general be sustained across a border between grains in different crystallographic orientations. A further implication is that plates of acicular ferrite, like bainite, *always* have an orientation relationship with the parent phase, which is within the Bain region.

1.2.7 Martensite formation:

Martensite is a product of diffusionless transformation. In welds, it forms in the small amount of residual austenite that remains after the higher temperature products have formed. The martensite in normal low alloy steel weld deposits occurs only in small quantities, mostly limited to the regions which are called microphases, which also contain some retained austenite. In certain high strength welds it is possible to have microstructures with large quantities of martensite but the carbon concentration must then be kept very small to avoid hydrogen cracking (Svensson and Bhadeshia, 1988).

1.3 Overall Model of Weld Microstructure

The microstructure evolution as a function of transformation temperature is shown schematically in Fig. 1.8. The flow chart describing the weld microstructure model is given in Fig. 1.9.

1.3.1 Weld Cooling Curve

The nature of heat flow in welding is two dimensional or three dimensional (or indeed an in between case). At temperatures, below melting point of the fusion zone, the cooling rate is virtually independent of the position (AWS, 1981). An equation of the form

\[
dT / dt = \left( C_1 / Q \right) (T - T_i) ^ {C_2}
\]

(1.7)
can then be used empirically to represent the weld metal cooling rate, with \( C_1, C_2 \) taken to be adjustable constants obtained by fitting the experimental data (Svensson *et al.*, 1986). \( T_i \) is the interpass temperature, \( T \) is temperature of interest and \( Q \) is the heat input given to the weld (see equation 1.1).

1.3.2 Characteristic transformation temperatures

The transformation temperatures are calculated using free energy change for transformation from austenite to ferrite. The free energy calculations are based on a method published
elsewhere (Shiflet et al., 1978, Aaronson et al., 1966a& b and Bhadeshia, 1980a, 1982a). Initiation of Widmanstätten ferrite and bainite necessitates a minimum driving force for nucleation \( \Delta G_{\text{max}} \) given by a universal \( G_N \) function. The \( G_N \) function was derived by fitting \( \Delta G_{\text{max}} \) with the published transformation temperature data of Steven and Haynes (1956). Another function which was based on \( \Delta G^{\gamma'\rightarrow\gamma+\alpha} \) was also derived. It was found that similar results were obtained by use of either one of the functions. The use of \( \Delta G_{\text{max}} \) for nucleation of displacive products may suggest that the nucleation may involve partitioning of carbon, during displacive transformation to Widmanstätten ferrite and bainite. And this may not be operative in the growth stage. The transformation temperatures should consider the growth conditions. Thus the following conditions are applicable for transformation start temperatures of Widmanstätten ferrite and bainite.

\[
\begin{align*}
\Delta G_{\text{max}} & \geq G_N \\
\Delta G^{\gamma\rightarrow\gamma'\rightarrow\gamma+\alpha} & \geq 50J \text{ mole}^{-1}
\end{align*}
\] for Widmanstätten ferrite (1.8)

Here the 50 J mole\(^{-1}\) is needed to satisfy the stored elastic transformation strain energy during transformation.

\[
\begin{align*}
\Delta G_{\text{max}} & \geq G_N \\
\Delta G^{\gamma\rightarrow\alpha} & \geq 400J \text{ mole}^{-1}
\end{align*}
\] for Bainitic ferrite (1.9)

Here 400 J mole\(^{-1}\) is needed to satisfy the stored elastic strain energy during bainitic transformation (Bhadeshia, 1981a).

For martensitic start temperature a minimum free energy change has to be met by \( \Delta G^{\gamma\rightarrow\alpha} \) for a given temperature (Bhadeshia, 1981c&d). The minimum free energy change has been given by following equation.

\[
\Delta G_{\{M_s\}_{\text{minimum}}} = -1120.00 - f(\bar{x}_c) \text{ J mole}^{-1}
\] (1.10)

\[
f(\bar{x}_c) = 10568.0\bar{x}_c + 94.1
\] (1.11)

where \( \bar{x}_c \) is the mean carbon concentration in mole fraction.

1.3.3 Prediction of TTT diagrams

The methodology for this was developed by Bhadeshia (1982a). The time-temperature-transformation diagram is represented as two "C" curves, in which one represents reconstructive and the another displacive transformation. Given a chemical free energy change for nucleation \( \Delta G_{\text{max}} \) of ferrite, the incubation time to achieve a detectable degree of transformation can be estimated. The equation for predicting the transformation time is after Russell's (1969) expression. The final form is as follows;
\[ \tau \propto \frac{T}{(\Delta G_{max}^v)^p D} \]  

(1.12)

where \( p \) is constant and \( \Delta G_{max}^v = \Delta G_{max}/V^m \), where \( V^m \), is the molar volume of ferrite. \( D \) is a diffusion coefficient related to boundary or volume diffusion, depending upon the state of the coherency of the nucleus. This can be represented by an activation energy term as given below.

\[ D = D_0 \exp\{-Q/RT\} \]  

(1.13)

\( T \) is the temperature in Kelvin and \( p \) an exponent whose magnitude is a function of the nature of of the nucleus (Russell obtained a value of 2 for coherent nucleus and 3 for an incoherent state). In line with Bhadeshia (1982a), by substituting an expression for the term \( D \), the final form of equation is as following:

\[ \tau = T^a(\Delta G_{max})^b \exp\{c/T\}.d \]  

(1.14)

where \( a, b, c \& d \) were found by fitting the equation to published experimental data. Data were taken from BISRA (1956) atlas of isothermal transformation diagrams. This approach considers the effect of alloying elements through a modification in the value of \( \Delta G_{max} \). Thus, the calculation procedures can be extended to the unknown situations, as long as the effect of alloying addition on free energy modification is known. Note that there is no accounting for the austenite grain size, but as pointed out by Bhadeshia (1982a) this is reasonable for the very early stages of transformation.

1.3.4 Columnar austenite grain size

In the model developed for the prediction of the primary weld metal microstructure for Fe-Mn-Si-C weld deposits by Bhadeshia et al., (1985) and modified by the work of Svensson et al., (1986), the columnar austenite grain size has to be measured or calculated using an empirical correlation based on the heat input to the \( (Q, \text{see equation 1.1}) \) weld and the compositions in wt.\%. The equation can calculate the mean linear intercept (on a transverse section in an orientation normal to the major axes of the columnar grains, \( L_{tn} \)) of the prior austenite grain size for any heat input \( (Q) \) and also weld metal composition (only for manganese, silicon and carbon):

\[ L_{tn}(\mu m) = 64.5 - 445.8(\text{wt.\%C}) + 138.6(\text{wt.\%Si}) - 7.581(\text{wt.\%Mn}) + 16(Q, kJ \text{ mm}^{-1}) \]  

(1.15)
The mean linear intercept was then used to calculate the side length ($a$) of the hexagonal prism, which represents a columnar austenite grain in the microstructure model. The relation between $L_{tn}$ and the side length of a hexagonal cross section is given by:

$$L_{tn}(\mu m) = \pi a \cos\{30^\circ\}/2$$

(1.16)

The above relation (1.15) is empirical in nature. The equation was derived by multiple regression of the grain size, composition and heat input data. It is not yet possible to predict the austenite grain size from fundamental principles; even the factors controlling it are far from clear (Bhadeshia, 1989). For example, during solidification, those grains with their $<100>$ directions most parallel to the direction of steepest temperature gradient grow rapidly, stifling the grains which are not suitably oriented. Consequently, the crystallographic texture of the parent plate, and the plane of that plate on which the weld is deposited, must influence the final austenite grain structure. Clear differences in the austenite grain structure were found between three welds deposited on mutually perpendicular faces of the same sample (Babu et al., 1991).

1.3.5 Microstructure Calculation Procedure

After the calculation of weld cooling characteristics, austenite grain size, TTT diagrams, characteristic transformation temperatures and the paraequilibrium phase boundaries of a particular alloy composition, the overall calculation of microstructure can begin (Fig. 1.9). The transformation to allotriomorphic ferrite starts first (Fig. 1.8). Using the TTT data and the additive reaction rule (equation 59.9 of Christian, 1975), the temperature at which allotriomorphic ferrite begins ($T_\alpha$) can be predicted. The model assumes that the austenite grain boundaries are uniformly covered by allotriomorphic ferrite, the instant weld cools to $T_\alpha$.

The allotriomorphic ferrite then is assumed to grow, as the weld cools from $T_\alpha$ to a temperature $T_C$, the temperature at which the reconstructive 'C' and displacive 'C' curves of TTT diagram intersect as illustrated in Fig. 1.10. To allow for continuous cooling, earlier isothermal growth equation (1.4) was differentiated with respect to time and assuming the variation of parabolic thickening rate to be negligible;

$$dq = 0.5\alpha_1 t^{-0.5} dt$$

(1.17)

Now integrating the above equation with respect to the total time spent on allotriomorphic ferrite reaction say $t_1$ (time taken to cool from $T_\alpha$ to $T_C$),

$$q = \int_{t=0}^{t_1} 0.5\alpha_1 t^{-0.5} dt$$

(1.18)
Once the thickness is found, assuming a hexagonal prism for the shape of the austenite grain and for a given austenite grain size, the volume fraction of allotriomorphic ferrite can be calculated using principles of stereology (Underwood, 1970).

\[ v_\alpha = 2q \tan\{30^\circ\}(2a - 2q \tan\{30^\circ\})/a^2 \]  

where \( a \) is the hexagon side length of the austenite grain and \( q \) is the half thickness of the allotriomorphic ferrite. The calculated volume fraction \( (v_\alpha) \), after an empirical correction \( (V_\alpha) \{(1.19)} \) as given below, was found to match very well with experimental data.

\[ V_\alpha = 2.04v_\alpha + 0.035 \]  

(1.20)

As soon as the temperature \( T_C \) is reached, the reconstructive transformation gives way to displacive transformation products. To start with, Widmanstätten ferrite emanates from the grain boundary allotriomorphic ferrite. It is important to note that the shape of Widmanstätten ferrite is such that the plate tip always advances into fresh austenite, so that it grows at a constant rate. The lengthening rate of Widmanstätten ferrite is found to be so high that the Widmanstätten ferrite can grow right across the austenite grain size in a fraction of second. The reaction can therefore be regarded as isothermal at \( T_C \). The volume fraction of Widmanstätten ferrite is calculated by considering the shape to be a triangular prism and given by;

\[ V_\omega = C_4 G(2a - 4q \tan\{30^\circ\})t_z^2/(2a)^2 \]

\( G \) is the growth rate of Widmanstätten ferrite calculated at the temperature \( T_C \), \( C_4 \) is a constant which is independent of the alloy composition and \( t_z \) is the time available for the growth of Widmanstätten ferrite. Widmanstätten ferrite nucleates from allotriomorphic ferrite from a side which exhibits rational orientation relation (KS/NW) with austenite. Hence only certain proportion of available \( \alpha/\gamma \) boundary area can be expected to develop into Widmanstätten ferrite. The constant \( C_4 \) thus incorporates the proportion of \( \alpha/\gamma \) boundary capable of nucleating Widmanstätten ferrite. The consideration of physical impingement with acicular ferrite gave a good agreement with experimental data. The impingement with acicular ferrite is taken into account by comparing with time interval, represented by \( t_e \), for the cessation of allotriomorphic ferrite growth and initiation of acicular ferrite reaction.

The amount of microphases \( (V_m) \) is calculated from knowledge of paraequilibrium phase diagram. By assum in welds, the transformation to allotriomorphic ferrite, Widmanstätten ferrite, and acicular ferrite occur to the maximum extent and by application of lever rule to \( \Delta e_1 \) and \( \Delta e_3' \) lines at \( M_s \) temperature. The volume fraction of acicular ferrite is calculated by difference;

13
\[ V_a = 1 - V_{\alpha} - V_W - V_m \]  

(1.21)

where \( V_a \) is the volume fraction of acicular ferrite, \( V_{\alpha} \) is the volume fraction of allotriomorphic ferrite, \( V_W \) is the volume fraction of Widmanstätten ferrite, \( V_m \) is the volume fraction of microphases.

It can be noted from the above equation that the maximum extent of transformation to acicular ferrite can be obtained by forcing \( V_{\alpha}, V_W \) to a very small value. In high alloy welds it leads to a mixture of acicular ferrite / bainite and martensite. Thus, it is important to model the kinetics of bainite / acicular ferrite in those circumstances (Rees, 1990). The calculation of the relative amount of various phases, has been extended by Sugden and Bhadeshia (1988a), for the prediction of the properties of the primary weld metal microstructure. The calculation is based on factorising the strength of weld metal due to various factors. The factors are: namely: strength of pure annealed iron, solid solution hardening and contribution from different microstructural morphologies like acicular ferrite, allotriomorphic ferrite and Widmanstätten ferrite. The weld model has shown considerable reliability for welds of most of the low alloy systems. The present research project was initiated on application of the model to Fe-Cr-Mo-C steel welds.

1.4 Chromium - Molybdenum Steels

Chromium - molybdenum steels have been used in petroleum industry reactor vessels, mainly to reduce corrosion by sulphur and its compounds which are present in crude oil. Their improved oxidation resistance and high temperature strength extended their application to other areas, like steam generators and heaters. Recently, they have also been used in hydro-treating vessels in the petroleum industry, where they are exposed to high temperatures and also high pressures of hydrogen. The service temperature is between 400 °C to 570 °C(Lundin et al., 1986, AWS Vol. 4). The steels are used in two states, namely in the quenched and tempered condition but mostly in the normalised air cooled condition. The most widely used Cr - Mo steel is the so called 2.25Cr-1Mo wt.%. The microstructure is usually a mixture of allotriomorphic ferrite and bainite or completely bainite, with some retained austenite (Kar and Todd, 1982).

Cr - Mo steels can be welded by most welding processes, the choice being related to section thickness. To avoid embrittlement due to hydrogen, preheat or high heat input or the use of low hydrogen electrodes is suggested. For thin sections, preheat can be avoided. The filler metals used are of the same composition or slightly richer than that of the base metal. In case of using high chromium filler wires for the weld metal, for certain dissimilar composition joints, care should be taken not to expose the joints to very high temperatures. Such exposure to high
temperature (>500 °C) will enhance carbon migration from the low Cr region to the high Cr region. This produces a soft region near the heat affected zone of the weldments. The welds are usually post weld heat treated depending upon alloy content and section thickness. For example the weld metal consisting of low carbon (≈ 0.05 wt.%) need not be post weld heat treated (AWS, Vol. 4, 1972). The important properties of Cr-Mo steels and its welds to be considered are:

- creep strength,
- toughness,
- temper embrittlement resistance,
- hydrogen attack resistance,
- stress relief cracking resistance

The creep strength of these alloys depends mainly on the type and amount of carbide precipitate and its stability. It is found to be that the formation of coherent acicular Mo₂C carbides gives better creep properties with the ferrite microstructure grain size playing only a secondary role (Lundin et al., 1986). Nevertheless, the toughness depends upon the ferrite microstructural features. Thus optimum combination of creep strength and toughness is an important parameter to be considered for Cr-Mo steels, and consequently microstructural development is worth studying.

1.5 Prediction of Microstructure in Fe-Cr-Mo-C Welds

Evans (1986,1988) published results of microstructure in weld metals containing chromium (> 1.5 wt.%) and molybdenum (> 0.5 wt.%). The weld microstructure model predicted continued increase of acicular ferrite as a function of alloy concentration. In contradiction, in real welds the columnar austenite grains of steel transform into bainite instead of acicular ferrite. This is in spite of the presence of non-metallic inclusions, which serve to intragranularly nucleate the plates of acicular ferrite. This has been also reported by Lundin et al., (1986), McGrath et al., (1989) and Josefsson et al., (1987, 1989). The anomaly is explained schematically in Fig. 1.11.

It has been observed in the case of C-Mn steel welds that the optimum strength and toughness is obtained by maximising the acicular ferrite microstructure in the weld metal (Ito et al., 1982). It is also known that the bainitic microstructure is poor in toughness compared with that of acicular ferrite. Thus a re-introduction of acicular ferrite in these welds could lead to a substantial improvement in properties. Hence, the present research programme concentrated on a fundamental understanding of acicular ferrite and bainite transformation behaviour in these steel welds, as presented in Fig. 1.12.
Fig. 1.1 Modelling phase transformations in steels, in response to thermomechanical conditions (after Kirkaldy, 1991).
Fig. 1.2 The manual metal arc welding process (Gray and Spence, 1982).

Fig. 1.3 The variety of regions of a typical weldment. $T_p$ is the peak temperature experienced by a particular region. $Ac1$ and $Ac3$ are the dynamic transformation start and finish temperature from ferrite to austenite respectively.
Fig. 1.4 Schematic illustration of the mechanisms of reconstructive and displacive transformations. The lines connect corresponding directions (Bhadeshia, 1987b).
Fig. 1.5 Classification of various austenite to ferrite transformation products in steels based on transformation mechanisms.
Fig. 1.6 Illustration of the transformation conditions to allotriomorphic ferrite growth, in a Fe-Mn-C system, with local equilibrium at the interface. (a) Schematic illustration of composition profile ahead of the moving \( \alpha/\gamma \) interface. (b) Partitioning local equilibrium mode (PLE), (c) Negligible partitioning local equilibrium (NPLE). The line \( cd \) in all cases defines a tie-line whereas the point \( o \) represents the alloy composition namely \( \tilde{z}_c \) and \( \tilde{z}_{\text{Mn}} \).
Fig. 1.7 Illustration of the incomplete reaction with paraequilibrium phase diagram and a free energy vs composition diagram. The carbon composition of residual austenite increases, as the transformation to bainite proceeds. The $T_0$ phase boundary also considers the strain energy of ferrite (in case of bainite it is 400 J mole$^{-1}$).
Fig. 1.8 Transformation sequences explained with the help of a schematic CCT diagram for a steel weld. The microstructure transformation sequence as a function of temperature being (a) austenite with oxide inclusions, (b) allotriomorphic ferrite nucleation, (c) site saturation of allotriomorphic ferrite and growth into austenite grain, (d) nucleation and growth of Widmanstätten ferrite, (e) nucleation and growth of acicular ferrite on inclusions and finally rest of the austenite transforms into martensite.
Fig. 1.9 Flow chart for overall weld microstructure prediction model (after Bhadeshia et al., 1985).

Fig. 1.10 Schematic illustration of TTT diagrams, and the temperature at which the reconstructive transformation give way to displacive transformation products (after Bhadeshia et al., 1985).
Fig. 1.11 Schematic illustration of the discrepancy observed in predicted volume fraction of acicular ferrite as a function of solute concentration with published results of Evans (1986 & 1988). Acicular ferrite was replaced by bainite after a certain degree of alloying.
Prediction of Microstructure of Fe-Cr-Mo-C Steel Multirun Weld Deposits

- Assessment of available data from literature using existing model
- Experiments to reproduce the reported microstructure development behaviour in the primary weld metal region
  - Theoretical assessment

Transition from bainite to acicular ferrite

- Mechanism of bainite to acicular ferrite transition
- Austenite solute concentration ahead of interface effect
  - Allotriomorphic ferrite / austenite crystallography effect

Phase Transformation Model
- Effect of Cobalt on allotriomorphic ferrite transformation kinetics
- Effect of stress on Acicular ferrite Transformation

Feedback to complete weld model

Fig. 1.12 Overview of the present research programme.
Chapter 2

General Experimental Techniques

2.1 Alloys

The alloys used were mainly weld metals. The samples were machined from all weld metal test pieces. The weld itself was fabricated according to the international standard ISO2560 (Fig. 2.1). The weld geometry is compatible with the minimisation of dilution effects associated with the melting of the base plate. The weld metal was deposited using the manual metal arc welding technique. The parameters used are listed in Table 2.1 and the chemical composition in Table 2.2.

<table>
<thead>
<tr>
<th>Table 2.1 Welding process parameters.</th>
</tr>
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<tbody>
<tr>
<td>Welding voltage</td>
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<td>Welding current</td>
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<tr>
<td>Welding speed</td>
</tr>
<tr>
<td>Interpass temperature</td>
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<tr>
<th>Table 2.2 Weld metal composition in wt.% with the oxygen and nitrogen concentration being stated in parts per million by weight.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALLOY</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>80</td>
</tr>
<tr>
<td>79</td>
</tr>
<tr>
<td>78</td>
</tr>
<tr>
<td>77</td>
</tr>
<tr>
<td>A1</td>
</tr>
<tr>
<td>AM1†</td>
</tr>
</tbody>
</table>

†also contains 4.3 wt.% cobalt
2.2 Sample Preparation and Heat Treatments

The samples machined from the weld were hot-rolled and swaged to rods of 3 mm diameter and 15 mm length. Some of these cylindrical samples were subsequently drilled along the cylinder axes to give 1.5 mm diameter bores, in order to accelerate the cooling rate that could be achieved during dilatometric experiments. To minimise any effects of chemical segregation, the specimens were then homogenised by annealing at 1200 °C for 3 days while they were protected by sealing in quartz tubes each containing a partial pressure of pure argon. After annealing, the samples were quenched in an ice-water mixture.

The heat treatment studies were mostly carried out in electric resistance heated furnaces (accuracy ± 5 °C). Some of the rapid heat treatments were carried out using high speed dilatometry.

2.3 Dilatometry

The advantage of dilatometry is that it enables transformations to be recorded as they happen. The setup of the sample is explained schematically in Fig. 2.2. The temperatures were measured by a Pt/Pt-Rh thermocouple spot welded to the sample. The volume change associated with a phase transformation can be followed by monitoring the change in length, which over the temperature region of interest can provide information about the transformation temperatures and the reaction kinetics. The length change during transformation was recorded using a Theta Industries high-speed dilatometer which is equipped with a water cooled induction furnace which has an essentially zero thermal mass. The intermediate cooling of specimen in dilatometry was carried out using helium gas quench. The dilatometer has been interfaced with a BBC/Acorn computer which is used for programming the thermal cycles and also for automatically collecting and recording length change, time and temperature data. For the dilatometric studies the homogenised specimens were electroplated with 0.08 - 0.1 mm thick layer of nickel to avoid surface degradation and surface nucleation effects (Strangwood and Bhadeshia, 1987c).

The following method is used for calculation of volume fraction of ferrite transformed as a function of time in isothermal transformation studies. The volume fraction of transformation is related to the length change detected by the dilatometer. For bainitic transformation involving no precipitation of carbides, the relation is given by the following equation: (Bhadeshia, 1982b).

\[
\frac{\Delta L}{L} \approx \frac{2V a_\alpha^3 + (1 - V) a_\gamma^3 - a_\delta^3}{3 a_\gamma^3}
\]  

(2.1)

where
\( \Delta L \) is the relative length change due to transformation, \( V \) is the volume fraction of ferrite, \( a_\alpha \) is the lattice parameter of ferrite (a function of temperature), which is given by,

\[
a_\alpha = \bar{a}_\alpha (1 + \epsilon_\alpha (T - 298))
\]

where \( T \) is the absolute temperature, \( \bar{a}_\alpha \) is the lattice parameter of ferrite at ambient temperature (25 °C), \( \epsilon_\alpha \) is the linear thermal expansion coefficient of ferrite, \( \bar{a}_\gamma \) is the calculated lattice parameter of austenite at the mean alloy composition, i.e., when \( V = 0 \), it is given by,

\[
\bar{a}_\gamma = \left[ \frac{a_\gamma^0 + \sum_{i=1}^{n} C_i x_i}{1 + \epsilon_\gamma (T - 298)} \right] [1 + \epsilon_\gamma (T - 298)]
\]

where \( a_\gamma^0 \) is the lattice parameter of unalloyed austenite, \( \epsilon_\gamma \) is the linear thermal expansion coefficient of austenite, \( C_i \) are coefficients relating alloying element concentration, \( x_i \), to the lattice parameter, where \( i = 1, 2, \ldots, n \) denoting various alloying elements (\( i = 1 \) for carbon). \( a_\gamma \) is the calculated lattice parameter of austenite taking account of the carbon enrichment in austenite when \( V \neq 0 \) given by,

\[
a_\gamma = \left[ a_\gamma + C_1 \frac{(\bar{x} - V \bar{x}_C^0)}{1 - V} + \sum_{i=2}^{n} C_i x_i \right] [1 + \epsilon_\gamma (T - 298)]
\]

where \( \bar{x}_C^0 \) is assumed to be given by the equilibrium concentration of carbon in ferrite in Fe-C alloys, as estimated using an quasichemical thermodynamic model (Mclellan and Dunn, 1969, Bhadeshia, 1982c) and \( \bar{x} \) is the mean carbon concentration of the alloy in mole fraction. The above method of analysis will be used in the following chapters.

2.4 Lattice Parameters Measurement

The lattice parameter values necessary for the interpretation of dilatometric data were measured for ferrite from samples tempered at 600 °C for one hour, using the Debye-Scherrer X-ray diffraction method with Cu-K\(_\alpha\) radiation. The accelerating voltage was 45 kV and the tube current being 25 mA. As the Cu-K\(_{\alpha1}\) and Cu-K\(_{\alpha2}\) lines could not be resolved, an average wavelength of 1.5424 Å was used for the analysis. A specimen of 0.5 mm diameter was prepared by careful machining from a 3 mm diameter rod, and its surface layer was removed by soaking in a chemical polishing mixture of 5% HF and 50% H\(_2\)O\(_2\) and 45% H\(_2\)O for 10 min; this procedure leads to more accurate parameter measurements since the effects of deformation induced by machining are removed. The Bragg angles were measured from the 011, 002, 112, 022 and 013 reflections and the data plotted against the Nelson-Riley extrapolation function with a least squares linear regression procedure. Since errors decrease with increasing Bragg angle (\( \theta \)), the data were weighted using a \( \frac{1}{\cos^2 \theta} \) function during regression analysis (Cullity, 1978).
2.5 Metallography

2.5.1 Transmission electron microscopy - EDX

The thin foil sample preparation for transmission electron microscope studies was as follows; After slicing 3 mm diameter rods into thin discs of 0.3 mm thickness, the discs were thinned down to 60-80 μm by abrasion using SiC coated grinding paper, and electropolished using an electrolyte consisting of a mixture of 5% perchloric acid, 25% glycerol and 70% ethyl alcohol. The polishing potential was 65 V at a current of 18-25 mA, the electrolyte temperature range being 0-10 °C. The thin foils were examined using a Philips EM-300 or EM-400T transmission electron microscope operated at 100 kV and 120 kV respectively.

Thin film extraction carbon replicas were also prepared for some of the heat treated and weld samples. Replicas were prepared by vapour deposition of carbon on to the sample in a vacuum chamber. The carbon film was stripped off from surface of the sample, by etching away the matrix in 5% chloral (5% concentrated HCl in ethanol) solution. The replicas were mounted on to copper grids and were observed in TEM.

Thin film foils or replicas were mounted on to a low background specimen holder and tilted to 35° take off angle in the microscope column during energy dispersive X-ray analysis (EDX). The X-ray energy spectra was analysed by LINK - RTS2 analyser program. The program calculates the relative amount of elements present in a test by fitting observed energy spectrum to a standard spectrum. The program is also capable of deconvolving overlapping peaks and giving a thickness correction. The scattering effects in the specimen lead to a beam broadening and was estimated to be around 20 nm with the original spot size being around 2-5 nm.

2.5.2 Scanning Electron Microscopy - EDX

The samples were also imaged in a scanning electron microscope operated at 25 kV and equipped with an energy dispersive X-ray analyser. The specimen was tilted to a take off angle of 45°. The accelerating voltage was reduced to 20 kV for EDX analysis.

2.5.3 Light microscopy and microhardness testing

The sectioned specimens were mechanically polished down to 1 μm finish and etched in 2% nital. Volume fraction measurements were carried out using a Swift point counter at a magnification of 400× with 1000 points for each specimen.

The prior austenite grain size for heat treated samples was measured either directly on the metallographic samples when the boundaries were made clearly visible by layers of allotriomorphic ferrite or using a thermal grooving method. In the latter case, metallographically polished specimens were austenitised in a protective helium atmosphere in the dilatometer chamber, and the thermal grooves which develop as the grain boundaries and free surface tension terms
balance, can be used to reveal the positions of the grain boundaries. A micrograph of a thermal grooved specimen is given in Fig. 2.3. The grain sizes were defined using the usual mean linear intercept method. Samples were hardness tested in a Leitz-Vickers microhardness tester with a force of 0.981 N or in macro vickers hardness tester of 50 N load.

2.6 Thermomechanical Simulator

The heat treatment can easily be carried out in the Formaster thermomechanical simulator used in the present studies. The machine is equipped to simultaneously monitor and record the diametral and longitudinal strains, in addition to time, temperature and load data. It can be programmed to automatically carry out the specified thermomechanical treatments. The samples were in the form of 8 mm diameter cylinders 12 mm in length, made from the weld metal by rolling, swaging and machining (Fig. 2.4). The specimen was heated using a radio-frequency coil and the temperature was measured with a Pt/Pt-10%Rh thermocouple. The temperature variation along the length of the sample was checked to be within 4–5 °C. The simulator experiments were carried out with the specimen chamber filled with argon.
Welding joint design for all weldmetal test specimen corresponding to international standard, ISO 2560

Fig. 2.1 Illustration of all weld metal test specimen, used for preparation of welds, according to ISO 2560.
Fig. 2.2 Illustration of specimen set-up in dilatometer. The heating is by RF induction.

Fig. 2.3 Example micrograph showing the thermal grooving. The polished surface of alloy A78 (see Table 2.2) was austenitised at 1000°C for 10 minutes and cooled rapidly below the bainitic transformation temperature (530 °C).
Fig. 2.4 Illustration of specimen set-up in thermo mechanical simulator. The radius change is measured by laser interferometry, the relative length change is measured from the movement of the crosshead.
Chapter 3

The Microstructure of Fe-Cr-C Weld Metals

3.1 Introduction

The effect of systematically increasing only the chromium and molybdenum concentration in the weld metal has been studied quantitatively by Evans (1988, 1986). He found that as the concentration of either of these elements is increased, the amount of allotriomorph ferrite decreases. The volume fraction of acicular ferrite, however, goes through a maximum. The volume fraction of the remainder of the microstructure, which Evans described as "ferrite with aligned second phase" therefore increases with concentration. This effect is illustrated in Fig. 3.1. The ferrite with aligned second phase actually refers to either or both of bainite and Widmanstätten ferrite. The original diagram by Evans (1988, 1986), has been divided into two regions namely (A) and (B) to illustrate the point that the reduction in \( \alpha_a \) may actually arise because acicular ferrite is in increasing quantities replaced by bainite (B). This is supported by the fact that Fe-2.25Cr-1Mo wt.% weld deposits used in the power generation industry exhibit a bainitic structure in the as-deposited condition in spite of the presence of numerous nonmetallic inclusions (Lundin et al., 1986, McGarth et al., 1989 and Josefsson et al., 1987).

This chapter describes an analysis of the published results on Fe-Cr-C welds by Evans (1988) using the weld model developed by Bhadeshia et al., (1985). The second part of the chapter summarises the results of a microstructure study of a series of welds containing chromium. The aim has been to reproduce the behaviour reported by Evans. Observations of the primary weld metal microstructure using transmission electron microscopy are also presented.

3.2 Analysis of Published Data

The welding variables used for microstructural study by Evans (1988) are presented in Table 3.1 & 3.2. The microstructure results were reported for 1.03 wt.% and 1.85 wt.% Mn levels, for a variation of Cr concentration from 0 \( \rightarrow \) 2.3 wt.% . The weld model needs, in addition to the data presented in Table 3.1 and 3.2, the prior austenite grain size \( (L_{\text{mn}}) \) of the welds (see section 1.3.4). The empirical relation developed for the model is only applicable for Fe-Si-Mn-C welds. The results of Evans (1988) did not contain any data on austenite grain size. Hence, the empirical equation (1.15) was applied, by assuming the effect of chromium on the austenite grain size to be minimal.

A comparison of the calculated volume fractions of allotriomorph ferrite, Widmanstätten ferrite, and acicular ferrite \( \xi \) presented in Fig. 3.2. The figure indicates the poor correlation
Table 3.1 Welding process variables (from Evans, 1988).

<table>
<thead>
<tr>
<th>Variables</th>
<th>21 Volts</th>
<th>170 Amps</th>
<th>0.0027 m s⁻¹</th>
<th>250 °C</th>
<th>MMA</th>
</tr>
</thead>
</table>

Table 3.2 Weld metal composition (in wt.%).

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Mo</th>
<th>Cr</th>
<th>O/ppm</th>
<th>N/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>0.037</td>
<td>0.31</td>
<td>1.03</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E2</td>
<td>0.041</td>
<td>0.32</td>
<td>1.01</td>
<td>0.0</td>
<td>0.0</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E3</td>
<td>0.043</td>
<td>0.31</td>
<td>0.95</td>
<td>0.0</td>
<td>0.0</td>
<td>0.53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E4</td>
<td>0.045</td>
<td>0.32</td>
<td>0.97</td>
<td>0.0</td>
<td>0.0</td>
<td>1.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E5</td>
<td>0.046</td>
<td>0.30</td>
<td>0.93</td>
<td>0.0</td>
<td>0.0</td>
<td>2.38</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E6</td>
<td>0.045</td>
<td>0.33</td>
<td>1.85</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E7</td>
<td>0.048</td>
<td>0.33</td>
<td>1.85</td>
<td>0.0</td>
<td>0.0</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E8</td>
<td>0.051</td>
<td>0.33</td>
<td>1.83</td>
<td>0.0</td>
<td>0.0</td>
<td>0.53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E9</td>
<td>0.052</td>
<td>0.33</td>
<td>1.81</td>
<td>0.0</td>
<td>0.0</td>
<td>1.08</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E10</td>
<td>0.054</td>
<td>0.33</td>
<td>1.72</td>
<td>0.0</td>
<td>0.0</td>
<td>2.32</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

†Oxygen concentration and nitrogen concentration were taken as 300 ppm and 100 ppm respectively for the calculations. The estimated prior austenite grain size for welds E1-10 was in the range of 140-150 μm using the equation 1.15.

obtained in prediction of the allotriomorphic ferrite and acicular ferrite. The deviation is evident in high Cr welds, where the transition from acicular ferrite to bainite was observed.

3.3 Experimentation

The transition from acicular ferrite to bainite can be attributed to either a reduction
in austenite grain size (Yang and Bhadeshia, 1987a) or a change in inclusion characteristics (Harrison and Farrar, 1981). The analysis of the above parameters were not reported by Evans (1988). Thus, the present work concentrated on study of austenite grain size and inclusion characteristics in a series of Cr welds. All weld metal test pieces were fabricated (Table 2.1) with different chromium levels using the procedure described in chapter 2. The Cr content in weld was varied from 0.48 wt.\% (Table 2.2). Optical microscopy and scanning electron microscopy were used to characterise the microstructure, in transverse sections of the welds. Measurements of the prior austenite grain size were carried out by drawing test lines perpendicular to the major axes of the columnar grains, consistent with the approach of Svensson et al., (1986). The delineation of prior austenite grain boundaries by allotriomorphic ferrite made their identification relatively easy. In alloy 77, the austenite grain boundaries were very faint in the absence of allotriomorphic ferrite.

Specimens of the primary microstructure, were prepared as thin foils for transmission electron microscopy. Around 20 inclusions were microanalysed from each weld. Carbon film extraction replicas were used to measure the inclusion size distributions (100 inclusions per each weld).

3.4 Results and Discussion

3.4.1 Austenite grain size variation with chromium content in weld

The columnar austenite grain structures of the welds are shown in Fig. 3.3 and quantitative data in Fig. 3.4. The austenite grain size appears to increase with the chromium concentration, although the variations are in fact within the standard deviation given in Table 3.3. The small grain size of alloy 77 can in fact be attributed to its larger carbon concentration (equation 1.15) rather than to its chromium concentration. Thus, it has to be concluded that the changes in austenite grain sizes cannot explain the peak in $\alpha_a$ content as the chromium concentration is increased.

3.4.2 Weld Metal Microstructure

It is evident from Fig. 3.5 that as the chromium content increases, the amount of acicular ferrite increases at the expense of allotriomorphic ferrite. However, after 1 wt.\% Cr level the microstructure became very fine. The optical microstructure in alloy 77 indicated the presence of parallel sheaves of fine plates in most of the regions, consistent with Evans' (1988) results. It was found that the calculated volume fraction of allotriomorphic ferrite (Bhadeshia et al., 1985) was always greater than that measured (Table 3.4). The weld model predicted correctly the absence of allotriomorphic ferrite in alloy 77. In alloy 78, allotriomorphic ferrite was found to be discontinuous whereas the calculations are based on the assumption of uniformly covered
Table 3.3 Comparison of austenite grain sizes.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>Mean Linear Intercept $L_{tn}$ in μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
</tr>
<tr>
<td>80</td>
<td>91</td>
</tr>
<tr>
<td>79</td>
<td>97</td>
</tr>
<tr>
<td>78</td>
<td>110</td>
</tr>
<tr>
<td>77</td>
<td>85</td>
</tr>
</tbody>
</table>

Continuous Cooling Transformation (CCT) diagrams are useful in understanding the development of microstructure. Using the calculated TTT diagrams (Bhadeshia, 1982a), the CCT diagrams were estimated using the additive reaction rule for all the Cr welds (Fig. 3.6). The calculations represent the transformation start temperatures for different cooling rates. They indicate the inability of alloy 77 to form allotriomorphic ferrite for a typical cooling rate of 50 °Cs⁻¹. The sensitivity of allotriomorphic ferrite formation to the cooling rate can be seen from the CCT diagrams. Thus, the incomplete coverage of $\gamma$ boundaries by allotriomorphic ferrite observed in alloy 78 can be attributed to its higher hardenability. The weld model correctly predicts the observed trend in allotriomorphic ferrite fraction, although the accuracy could be improved. The amount of Widmanstätten ferrite decreased with increasing chromium concentration in a way consistent with the results of Bhadeshia et al., (1986c). Similar to Evans' (1988) results at high Cr concentration, the weld metal microstructure became finer. Transmission electron microscopy confirmed that alloys 80 and 79 contain acicular ferrite (Fig. 3.7). The plates nucleate from inclusions and probably also sympathetically from previously formed ferrite plates. Alloy 78 exhibited a mixed acicular ferrite and bainitic microstructure. Fig. 3.8a shows an acicular ferrite colony. Fig. 3.8b shows a dark field image of an acicular ferrite illustrating extensive dislocation networks. Figure 3.8c illustrates bainitic ferrite sheaves emanating from a prior austenite grain boundary. Alloy 77 showed a lesser tendency for acicular ferrite development, with considerable grain boundary nucleated bainitic ferrite (Fig. 3.8d). Figure 3.8e shows the sheaf structure of bainite comprising of many sub-units, a typical bainitic structure. Occasionally ferrite plates developing from inclusions were also observed (Fig. 3.8f), even in alloy 77.
Table 3.4 Microstructural constituents in the welds containing chromium.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>Microstructural component in %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
</tr>
<tr>
<td>exp.</td>
<td>calc.</td>
</tr>
<tr>
<td>80</td>
<td>25</td>
</tr>
<tr>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td>78†</td>
<td>5</td>
</tr>
<tr>
<td>77†</td>
<td>NO</td>
</tr>
</tbody>
</table>

exp. $\rightarrow$ experimental determination (point count analysis),
calc. $\rightarrow$ calculated using Bhadeshia et al., (1985) model,
$\alpha$ $\rightarrow$ allotriomorphic ferrite,
$\alpha_W$ $\rightarrow$ Widmanstätten ferrite,
$\alpha_a$ $\rightarrow$ acicular ferrite,
$\alpha_b$ $\rightarrow$ bainitic ferrite,
NC $\rightarrow$ not calculated.
NO $\rightarrow$ not observed
† difficulties in resolving the microstructure using optical microscopy.

The microstructural observations suggest a competition between grain boundary nucleated bainite and acicular ferrite (intragrannularly nucleated bainite) as a function of Cr. At high concentrations, the bainite reaction dominates. In other words, the formation of acicular ferrite is stifled by that of bainite as the Cr concentration increases.

The possible reasons for the above transition have to be explored, to design welding variables such that acicular ferrite can be introduced in high Cr welds. Bainitic ferrite is encouraged if the number density of grain boundary nucleation sites increases; acicular ferrite on the other hand is stimulated by an increase in the number density of intragrannular nucleation sites (inclusions). Thus, the transition may be related to a change in the relative number densities of inclusion and $\gamma$ grain boundary nucleation sites, or by some change in inclusions characteristics as the Cr concentration changes.

The measured inclusion compositions (Table 3.5) indicate no systematic or significant
Table 3.5 Comparison of mean inclusion composition determined by TEM-EDX on thin foils of the primary weld metal deposits in wt. %.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Si</th>
<th>Mn</th>
<th>Ti †</th>
<th>Al</th>
<th>Fe</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.4</td>
<td>20.5</td>
<td>41.5</td>
<td>6.3</td>
<td>1.1</td>
<td>30.1</td>
<td>2.0</td>
</tr>
<tr>
<td>79</td>
<td>1.1</td>
<td>20.5</td>
<td>36.5</td>
<td>5.7</td>
<td>1.2</td>
<td>32.8</td>
<td>1.6</td>
</tr>
<tr>
<td>78</td>
<td>0.9</td>
<td>21.7</td>
<td>40.5</td>
<td>5.4</td>
<td>1.7</td>
<td>28.3</td>
<td>1.7</td>
</tr>
<tr>
<td>77</td>
<td>1.5</td>
<td>14.6</td>
<td>36.1</td>
<td>8.7</td>
<td>1.8</td>
<td>36.7</td>
<td>0.9</td>
</tr>
</tbody>
</table>

† Maximum amount of titanium present in the inclusions were 15, 13, 16 and 25 wt.% in alloy 80, 79, 78 and 77 respectively.

change within the alloys studied. It can be deduced that the inclusions are complex silico-manganese oxides (the high concentration of iron may be an effect due to interference from the matrix during microanalysis). Relatively few inclusions were found to be rich in titanium. The inclusion number density is usually related to the oxygen present in the welds (Harrison and Farrar, 1981), which does not vary much (Table 2.2). Hence, a change in number density or size distribution is not expected. A detailed analysis of inclusions is summarised in Fig. 3.9 and Fig. 3.10. This reveals no change in the inclusion characteristics.

3.5 Summary

Published data on the effect of Cr and Mo on the primary weld microstructure have been analysed and it has been suggested that the reported “ferrite with second phase” at higher Cr levels is mainly bainitic ferrite. The weld model correctly predicts the experimental trend. Deviation from the microstructure model is found to be most marked at higher Cr concentration levels.

It has been demonstrated that the microstructure at higher Cr levels is bainitic in nature. There is a competition between intragranular nucleation and grain boundary nucleation; the latter dominates at higher Cr levels. No significant changes in austenite grain size and the inclusion characteristics were observed. In summary, the transition from acicular ferrite to bainite, observed as a function of Cr in welds, can neither be related solely to the austenite grain size, nor to any change in the inclusion characteristics. The indications are therefore that there must be an increase in the grain boundary nucleation of bainite, as the Cr concentration is increased. This hypothesis is investigated in detail in chapter 4.
Fig. 3.1 Illustration of the effect of chromium and molybdenum on C-Mn primary weld metal microstructure (Evans, 1988, 1986). The region "ferrite with second phase", is divided into two regions to indicate the expected behaviour. The region "B" represents bainite. (a) effect of Cr, (b) effect of Mo.
Fig. 3.2 Comparison of published data (Evans, 1988) with calculated microstructures. “Ferrite with second phase” (terminology of Evans) is represented as Widmanstätten ferrite, for comparison only. The classification of microstructure as ferrite with second phase at high Cr levels is not correct, as the microstructure becomes bainitic. The arrows in the case of acicular ferrite and Widmanstätten ferrite comparison correspond to the state of high Cr, where the microstructure is essentially bainitic.
Fig. 3.3 Comparison of the austenite grain structure development in the primary weld metal region as chromium content increases. Note the fine microstructure development in the case of alloy 77 and reduced grain boundary allotriomorphic ferrite delineation for alloy 78. (a) Alloy 80, (b) Alloy 79, (c) Alloy 78, (d) Alloy 77.
Fig. 3.3 continued....
Fig. 3.4 Prior austenite grain size ($\bar{L}_{in}$) for different weld Cr concentrations.
Fig. 3.5 Comparison of the primary weld metal microstructure as the chromium content increases; (a) Alloy 80, (b) Alloy 79, (c) Alloy 78, (d) Alloy 77.
Fig. 3.5 continued...
Fig. 3.6 Comparison of CCT diagrams from TTT data calculated using the method developed by Bhadeshia (1982a). The two cooling curves shown are for 5 °C s\(^{-1}\) and 50 °C s\(^{-1}\). The CCT diagrams were calculated using the additivity reaction rule (Christian, 1975)
Fig. 3.7 Comparison of the primary weld metal microstructures of alloy 80 and alloy 79.

(a) Acicular ferrite microstructure (arrow marks the region of possible sympathetic nucleation).

(b) Acicular ferrite colony in alloy 79. Sympathetic nucleation is again evident.
Fig. 3.8 Comparison of the primary weld metal microstructures of alloy 78 and alloy 77.

(a) Acicular ferrite colony in the weld metal region of alloy 78.

(b) Centered dark field image, using a (110) reflection of an acicular ferrite plate with a high dislocation density (alloy 78).
Fig. 3.8 continued...

(c) Bainitic ferrite sheaf emanating from a prior austenite grain boundary (alloy 78).

(d) Bainitic ferrite sheaf emanating from a prior austenite grain boundary (alloy 77).
Fig. 3.8 continued...

(e) Another example of a bainitic sheaf structure in alloy 77.
(f) Bright field transmission electron micrograph of acicular ferrite plate in alloy 77. Direct nucleation on an inclusion can be observed.
Fig. 3.9 Comparison of the size distributions of inclusions in the weld, illustrating no apparent change with the Cr concentration.
Fig. 3.10 Comparison of the number density of inclusions in the weld, illustrating no apparent change with the Cr concentration. The units on the 'X' axis correspond to the number of inclusions per unit area measured in extraction replicas.
Chapter 4

The Transition from Bainite to Acicular Ferrite in Reheated Fe-Cr-C Weld Deposits

4.1 Introduction

In many steel weld deposits, a reduction of allotriomorphic ferrite and Widmanstätten ferrite leads to a corresponding increase in the amount of acicular ferrite. This behaviour has been demonstrated to be consistent with phase transformation theory. It has been suggested however, that there is a peculiarity in the development of microstructure in Fe-Cr-Mo-C weld deposits (Bhadeshia, 1989, Evans, 1988 & chapter 3). The bainitic microstructure was observed at high alloy contents (see Fig. 3.1). In the previous chapter on the microstructure development in Fe-Cr-C welds the transition from acicular ferrite to bainite was observed. †

Recent work on acicular ferrite (Yang and Bhadeshia, 1987a & Strangwood and Bhadeshia, 1987a) indicates that acicular ferrite appears to be intragranularly nucleated bainite, in which the development of aggregates of parallel plates (the classical sheaves of bainite) is suppressed by the hard impingement of acicular ferrite plates nucleating from adjacent sites. Thus, bainite sheaves develop when they can nucleate at the austenite grain surfaces, whereas the intragranularly nucleated bainite is, in effect, acicular ferrite. Thus, a reduction in inclusion density leads to a transition from acicular ferrite to bainite as demonstrated by Harrison and Farrar (1981). Alternatively, an increase in the density of austenite grain boundary nucleation sites leads to the same transition (Yang and Bhadeshia, 1987a). These studies emphasise the dependence of the transition on the relative amounts of austenite grain boundary and intragranular nucleation sites available when the weld metal reaches a transformation temperature below the bainite-start temperature $B_s$.

Based on this current knowledge on the factors favouring bainite versus acicular ferrite, it was considered that bainitic microstructure begins to dominate at high solute concentration, perhaps because the usual allotriomorphic ferrite layers then begin to diminish, leaving the austenite grain surfaces exposed for the nucleation of bainite. Therefore, the work reported here had the intention of identifying any role of allotriomorphic ferrite in the transition from a predominantly bainitic microstructure to one containing a large amount of acicular ferrite. Allotriomorphic ferrite grows as layers on the prior austenite grain boundaries and, since it is the first phase to grow on cooling from the austenite phase field, it should cause a reduction in the number density of austenite grain boundary nucleation sites and, hence, promote the

† Here the word transition means, the austenite instead of transforming to acicular ferrite transforms to bainitic ferrite.
preferential formation of acicular ferrite at the expense of bainite. This at first sight appears to be consistent with the behaviour of the Fe-Cr-Mo-C welds, if it is assumed that the Cr and Mo prevent the formation of allotriomorphic ferrite at high concentrations and, hence lead to the promotion of classical bainite at the expense of acicular ferrite.

4.2 Experimentation

4.2.1 Alloy

The samples were machined from the all weld metal test specimen of alloy 78 (Table. 2.2). The samples were prepared as per the procedure outlined in chapter 2. The controlled heat treatments carried out on this alloy are presented below.

4.2.2 Furnace Heat Treatments

The main aim of the present investigation was to study the influence of prior allotriomorphic ferrite formation on the austenite/austenite grain boundaries, on subsequent transformation below $B_s$. To plan the heat treatments, a phase diagram and a time-temperature-transformation (TTT) diagram was calculated for the alloy 78, the calculation taking into account of the C, Si, Mn, Ni, Mo and Cr concentrations, using a method published elsewhere (Bhadeshia, 1981a, 1982a). The bainitic ferrite ($B_s$), Widmanstätten ferrite ($W_s$), and martensitic start temperatures ($M_s$) were also calculated using the same method (Fig. 4.1). The equilibrium $A_{e3}$ transformation temperature was calculated as in Sugden and Bhadeshia (1989c). The transformation temperature data are presented in Table 4.1.

<table>
<thead>
<tr>
<th>Table 4.1 Calculated transformation data for alloy 78.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{e3}$, °C</td>
</tr>
<tr>
<td>$W_s$, °C</td>
</tr>
<tr>
<td>$B_s$, °C</td>
</tr>
<tr>
<td>$M_s$, °C</td>
</tr>
</tbody>
</table>

The experiments involved the isothermal reaction of austenite at two successive temperatures $T_1$ and $T_2$. The heat treatment at $T_1$ was intended to allow the formation of some allotriomorphic ferrite, so that the austenite grain boundaries would be covered by a thin layer of the ferrite. The remainder of the austenite could then be transformed at a temperature $T_2$ below $B_s$. For comparison, the heat treatment at $T_1$ was omitted for some samples, the austenite being quenched directly to $T_2$ to avoid the formation of any allotriomorphic ferrite.
Table 4.2 Details of the furnace experiments:

<table>
<thead>
<tr>
<th>Notation</th>
<th>$T_\gamma$</th>
<th>Time at $T_\gamma$</th>
<th>Time at $T_1$</th>
<th>Time at $T_2$</th>
<th>Quench Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>min</td>
<td>°C</td>
<td>min</td>
<td>minutes</td>
</tr>
<tr>
<td>F1</td>
<td>1150</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>500</td>
</tr>
<tr>
<td>F2</td>
<td>1150</td>
<td>20</td>
<td>700</td>
<td>5</td>
<td>500</td>
</tr>
<tr>
<td>F3</td>
<td>1150</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>470</td>
</tr>
<tr>
<td>F4</td>
<td>1150</td>
<td>30</td>
<td>800</td>
<td>10</td>
<td>470</td>
</tr>
<tr>
<td>F5</td>
<td>1150</td>
<td>30</td>
<td>800</td>
<td>5</td>
<td>470</td>
</tr>
<tr>
<td>F6</td>
<td>1150</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F7</td>
<td>1150</td>
<td>30</td>
<td>800</td>
<td>10</td>
<td>600</td>
</tr>
<tr>
<td>F8</td>
<td>1150</td>
<td>30</td>
<td>800</td>
<td>10</td>
<td>-</td>
</tr>
</tbody>
</table>

†The cooling rate could not be measured as the samples were sealed in the quartz tubes, but was estimated to be about 50 °C s⁻¹.

Based on the data from the calculated TTT diagram, heat treatments F1 and F2 were planned as described in Table 4.2; the prefix F refers to experiments carried out using a resistance heated furnace. Three furnaces were maintained at the required temperatures one for austenitising at a temperature $T_\gamma$ and the remaining ones for isothermal heat treatments at $T_1$ and $T_2$. During the heat treatments, the samples were transferred rapidly between furnaces. Preliminary studies revealed that owing to relatively low cooling rate associated with such transfers, allotriomorphic ferrite formation could not be avoided in specimen F1 while cooling from $T_\gamma$ to $T_2$. In addition, heat treatment at $T_1 = 700$ °C was found to lead to the rapid growth of allotriomorphic ferrite to a very large volume fraction ($\approx 0.75$) after only five minutes at $T_1$. This defeats the purpose of the experiment, which was to decorate the austenite grain surfaces with thin layers of ferrite which do not consume the bulk of the austenite, leaving it free to decompose into intragranularly nucleated acicular ferrite.

To overcome these difficulties, the driving force for allotriomorphic ferrite growth was reduced by raising $T_1$, and the cooling rate from $T_1$ to $T_2$ was increased by increasing further the difference $T_1 - T_2$ by reducing $T_2$ to 470 °C. These changes are not sufficient in themselves to prevent the formation of allotriomorphic ferrite in the interval between $T_1$ and $T_2$, but that is not important, providing a thin covering of allotriomorphic layer is observed at the austenite grain.
surfaces before $T_2$ is attained. The calculated data on the transformation behaviour expected for the present alloy (see Table 4.3), also suggest the scale of incubation time available at that particular temperature. The modified experiments (F3-F8) gave some results of interest which will be discussed below. The heat treatment schedules are shown schematically in Fig. 4.2

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>$x_c^{\alpha}$</th>
<th>$x_c^{\gamma}$</th>
<th>$D$ cm$^2$ s$^{-1}$</th>
<th>$\alpha_1$ cm s$^{-0.5}$</th>
<th>$\tau$ s</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.0029</td>
<td>0.00042</td>
<td>$0.117 \times 10^{-7}$</td>
<td>$0.262 \times 10^{-4}$</td>
<td>$0.51 \times 10^4$</td>
</tr>
<tr>
<td>760</td>
<td>0.0073</td>
<td>0.000542</td>
<td>$0.7628 \times 10^{-8}$</td>
<td>$1.526 \times 10^{-4}$</td>
<td>$0.26 \times 10^2$</td>
</tr>
<tr>
<td>720</td>
<td>0.0150</td>
<td>0.000633</td>
<td>$0.4416 \times 10^{-8}$</td>
<td>$2.204 \times 10^{-4}$</td>
<td>$0.5 \times 10^1$</td>
</tr>
<tr>
<td>680</td>
<td>0.0251</td>
<td>0.000698</td>
<td>$0.2375 \times 10^{-8}$</td>
<td>$2.321 \times 10^{-4}$</td>
<td>$0.43 \times 10^1$</td>
</tr>
<tr>
<td>640</td>
<td>0.0362</td>
<td>0.000738</td>
<td>$0.1291 \times 10^{-8}$</td>
<td>$2.157 \times 10^{-4}$</td>
<td>$0.88 \times 10^1$</td>
</tr>
<tr>
<td>600</td>
<td>0.0483</td>
<td>0.000754</td>
<td>$0.0668 \times 10^{-8}$</td>
<td>$1.838 \times 10^{-4}$</td>
<td>$0.39 \times 10^2$</td>
</tr>
</tbody>
</table>

$x_c^{\alpha}$ is the carbon concentration in austenite which is in paraequilibrium with ferrite at the temperature concerned, in units of mole fraction.

$x_c^{\gamma}$ is the carbon concentration in ferrite which is in paraequilibrium with austenite at the temperature concerned, in units of mole fraction.

$\alpha_1$ one-dimensional parabolic thickening rate constant for paraequilibrium growth of allotriomorphic ferrite.

$\tau$ is the incubation time needed for detectable degree of transformation to ferrite from austenite.

$D$ is the weighted average diffusivity calculated by considering the carbon concentration profile in front of the moving ferrite interface, as discussed before (section 1.2.3)

### 4.2.3 Dilatometry

The dilatometric experiments were directed towards the investigation of the “incomplete reaction phenomenon” of the type reported for acicular ferrite and bainite in weld alloys, by Yang and Bhadeshia (1987a) and Strangwood and Bhadeshia (1987a). This would help to verify that the transformation products which form at $T_2$ correspond to the reported thermodynamic characterisation of bainite or acicular ferrite. Samples were austenitised at two different temperatures (1000 °C for 10 minutes or 1150 °C for 10 minutes) to obtain a small or a large
austenite grain size to induce a predominantly bainite or acicular ferrite microstructure, respectively, when subsequently transformed isothermally below the calculated \( B_S \) temperature. Thus, the experiment was designed to change the relative number densities of austenite grain boundary versus intragranular nucleation sites. Some details of the dilatometric experiments are given in the Table 4.4. Dilatometric relative length change data was analysed to obtain volume fractions of transformation. The method outlined in section 2.3 was adopted.

<table>
<thead>
<tr>
<th>Experiment Notation</th>
<th>( T_\gamma ) ( ^\circ C )</th>
<th>Time at ( T_\gamma ) ( ) seconds</th>
<th>( T_i ) ( ^\circ C )</th>
<th>Time at ( T_\gamma ) ( ) minutes</th>
<th>( T_S ) ( ^\circ C )</th>
<th>( \Delta t_{850-T_i} ) ( ) seconds</th>
<th>Cooling condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1000</td>
<td>600</td>
<td>505</td>
<td>60</td>
<td>774</td>
<td>4.5</td>
<td>Quench</td>
</tr>
<tr>
<td>S2</td>
<td>1000</td>
<td>600</td>
<td>519</td>
<td>60</td>
<td>785</td>
<td>5.3</td>
<td>Quench</td>
</tr>
<tr>
<td>L1</td>
<td>1150</td>
<td>600</td>
<td>513</td>
<td>60</td>
<td>660</td>
<td>7.6</td>
<td>Quench</td>
</tr>
<tr>
<td>L2</td>
<td>1150</td>
<td>600</td>
<td>529</td>
<td>60</td>
<td>665</td>
<td>14.8</td>
<td>Quench</td>
</tr>
</tbody>
</table>

L,S denote the transformation from large and small austenite grain sizes respectively. The grain sizes measured for low \( T_\gamma \) and high \( T_\gamma \) samples were 41 \( \pm \) 5 \( \mu m \) \( (T_\gamma=1000 \, ^\circ C) \), 71 \( \pm \) 6 \( \mu m \) \( (T_\gamma=1150 \, ^\circ C) \) respectively as measured using the thermal grooving method.

4.2.4 Measurement of the linear thermal expansion coefficients

It is evident that a knowledge of the thermal expansion coefficients \( e_\alpha \) and \( e_\gamma \) is necessary for computing the volume fraction of transformation as a function of the dilatometric length change. To measure the expansion coefficient of ferrite, dilatometer specimens were first tempered for one hour at 600 \( ^\circ C \) to ensure an essentially ferritic microstructure. The length change data recorded during slow heating to 600 \( ^\circ C \) and cooling from 600 \( ^\circ C \) \( (\approx 4 \, ^\circ C \, s^{-1}) \) were then analysed to estimate the linear expansivity.

For austenite, length change data during heating from 850 to 1000 \( ^\circ C \), at a rate of 10 \( ^\circ C \) \( s^{-1} \), in the austenite phase field were analysed. The expansion coefficients measured in this way (Fig. 4.3) were found to be:

\[ e_\alpha = 1.4026 \times 10^{-5} \pm 0.35 \times 10^{-7} \, ^\circ C^{-1} \] and \[ e_\gamma = 1.8854 \times 10^{-5} \pm 0.12 \times 10^{-7} \, ^\circ C^{-1} \].

These values were constant over the temperature ranges studied, as indicated by correlation coefficients greater than 0.99 when the length change versus temperature data were subjected
to linear regression analysis.

4.2.5 Lattice parameters

The lattice parameter values are necessary for the interpretation of dilatometric data. The procedure outlined in section 2.4 was adopted. The extrapolation procedure to obtain the lattice parameter is shown in Fig. 4.4. The ferrite lattice parameter was found to be $2.8679 \pm 0.106 \times 10^{-2}$ Å. The predicted lattice parameter using the relations given by Leslie (1982) and Wever (1928) and using a program which again takes into consideration the equilibrium dissolved carbon in ferrite, (Bhadeshia et al., 1990) the lattice parameter of ferrite was calculated and found to be 2.8679 Å, which is in remarkable agreement with the experimental value. The equation for predicting the ferrite lattice parameter is as given below.

$$
\bar{a}_a = a_{Fe}^0 + \varepsilon_c - (3.0 \times 10^{-12})M_{Si} + (6.0 \times 10^{-12})M_{Mn}
+ (7.0 \times 10^{-12})M_{Ni} + (0.31 \times 10^{-10})M_{Mo}
+ (5.0 \times 10^{-12})M_{Cr} + (0.096 \times 10^{-10})M_{V}
$$

where $M_{Si,Mn,Ni,Mo,Cr,V}$ are mole fractions of alloying elements. $a_{Fe}^0$ is the lattice parameter of pure iron taken to be 2.8664 Å, $\varepsilon_c$ is the expansion in lattice parameter due to carbon dissolved in the ferrite.

4.2.6 Microscopy

The microstructures were observed using optical microscope, scanning electron microscope (SEM) and transmission electron microscope (TEM). The specimen preparation techniques were outlined before (see chapter 2). Some of the selected samples were analysed by energy dispersive X-ray analysis in SEM and in TEM. The prior austenite grain size was measured by thermal grooving and hardness tests were carried out on the heat treated samples.

4.3 Results

4.3.1 Effect of allotriomorphic ferrite

The microstructures obtained in samples F3-5 and corresponding transmission electron micrographs of selected specimens are shown in Fig. 4.5. The microstructures obtained in samples F6-8 and a transmission electron micrograph of sample F6 are shown in Fig. 4.6

The optical microstructure of specimen F3 revealed classic bainite sheaves, consisting of aggregates of small parallel plates, a result confirmed using transmission electron microscopy (Fig. 4.5d & e); this was the expected result, i.e., all platelets within a sheaf have identical crystallographic orientation (Bhadeshia and Edmonds 1979, 1980). This is consistent with the fact
that the sample had been transformed directly to bainite without the intervening isothermal hold at $T_1$, which would have caused the formation of allotriomorphic ferrite; thus the bainite sheaves nucleate at the undecorated austenite grain boundaries. In contrast, samples F4 and F5 which had been given a two-stage heat treatment, showed very different final microstructure, consisting of layers of allotriomorphic ferrite and intragranularly nucleated acicular ferrite (Fig. 4.5b,c & f). The allotriomorphic ferrite destroys the original austenite grain boundary nucleation sites and thereby forces heterogeneous nucleation of acicular ferrite on intragranular inclusions.

To demonstrate that such drastic changes in microstructure cannot be explained by austenite grain size variations in the present studies, the austenite grain sizes of specimens F5 and F6 were measured and found to be $70 \pm 10 \, \mu m$ for F5 and $76 \pm 11 \, \mu m$ for F6. As expected, the measurements are identical within the limits of the experimental error. The apparent thickness of allotriomorphic ferrite of about 5-10 $\mu m$ when compared with the austenite grain size shows that, for most of the cases studied, there is sufficient austenite remaining for further transformation at $T_2$, a condition essential for the intragranular formation of acicular ferrite.

Further experiments were carried out to confirm that acicular ferrite does not form in this alloy unless the transformation temperature $T_2$ is less than $B_S$. Specimen F7 was first transformed partially to a similar amount of allotriomorphic ferrite at $T_1 = 800 \, ^oC$ in the usual way and was then quenched to a higher value of $T_2 = 600 \, ^oC$ which is above $B_S$. The microstructure obtained (Fig. 4.6c) shows clearly that transformation above $B_S$ leads simply to the formation of more allotriomorphic ferrite, while any small amount of untransformed austenite decomposes martensitically on cooling to ambient temperature. The microstructure consists essentially of equiaxed allotriomorphic ferrite and small islands of martensite which would have formed on quenching after the second isothermal heat treatment. The results were confirmed further by sample F8, (Fig. 4.6d) which was quenched without any second isothermal heat treatment; allotriomorphic ferrite is again observed as for F7 (or F4,5) but its volume fraction is found to be lower than in F7 due to the absence of the isothermal reaction at 600 $^oC$. The residual austenite has again transformed into martensite instead of acicular ferrite. The result supports the concept that the acicular ferrite microstructure does not form by transformation above $B_S$.

The volume fractions of allotriomorphic ferrite in samples F4 and F5 were measured to be 0.33 and 0.46, respectively. The calculated equilibrium volume fraction of allotriomorphic ferrite, that can form at 800 $^oC$ was found to be 0.20, based on application of the lever rule to the paraequilibrium phase diagram. The thickness of allotriomorphic ferrite that can grow, assuming paraequilibrium carbon diffusion controlled growth, at a given temperature can be
calculated using the following equation (Bhadeshia et al., 1985):

\[ q = \alpha_1 \times t^{0.5} \]  

(4.2)

where \( q \) is the half thickness of allotriomorphic ferrite, \( \alpha_1 \) is one-dimensional parabolic thickness of ferrite thickness of ferrite and \( t \) is the time in seconds.

The calculation using the above equation indicates that, for a holding time of 10 minutes after the initiation of allotriomorphic growth, the thickness of ferrite should be around 6.42 \( \mu \text{m} \). As seen in the Table 4.3, the time needed for a detectable amount of transformation is much higher relative to the time at \( T_1 \). Thus, some of the ferrite might have formed while cooling from 800 °C to \( T_2 \). Therefore, it is not possible to control the allotriomorphic ferrite reaction because of the low hardenability used. However, this does not affect the concept of the experiment, providing that the amount of allotriomorphic ferrite that forms before bainite reaction is not excessive. The fact that the allotriomorphic ferrite forms during continuous cooling within the range \( T_1 - T_2 \) is of no consequence, as demonstrated by sample F6, which was cooled continuously from the austenite phase field by keeping the specimen within a sealed quartz tube and holding it in an ice water mixture. This yielded a microstructure in which the austenite grain surfaces were decorated by thin layers of allotriomorphic ferrite layer and acicular ferrite (Fig. 4.6a and 4.6b). The similarity of the microstructure to that observed in the as deposited layers of ordinary C-Mn welds is considerable. The result emphasises the destruction of austenite grain boundary nucleation sites by allotriomorphic ferrite and shows its indirect effect in promoting the transformation of the remaining austenite to acicular ferrite.

EDX analysis (samples F6 and F5 in TEM and SEM, respectively) revealed no discernible change in the bulk substitutional alloying element concentration during allotriomorphic ferrite growth (See Table 4.5) within the experimental error. The areas which were subjected to EDX analysis in TEM and SEM are shown in Fig. 4.7. The figure also shows the variation of Cr, Mn and Si across the allotriomorphic ferrite. This indicates that the allotriomorphic ferrite has inherited the original substitutional alloying element concentration, consistent with a paraequilibrium growth mechanism (see section 1.2.3). The carbon extraction replicas have failed to show any presence of carbides in the transformed samples. This supports the assumption, made in deriving the relation between the length change and volume fraction of ferrite transformed (equation 2.1), the transformation to bainite is associated with no precipitation of carbides. The replicas were found to contain only inclusions (as the samples were originally taken from weld metal portion) of complex manganese, silicon oxides Table 4.5 also gives a summary of EDX analysis on inclusions in the sample F5.
Table 4.5 Results of microanalysis tests on allotriomorphic-acicular ferrite regions and inclusions in some of the furnace experiments.

<table>
<thead>
<tr>
<th>Alloying Element</th>
<th>Sample</th>
<th>Observed Concentration (mean) wt.%</th>
<th>Standard Deviation</th>
<th>Matrix Concentration in wt.%</th>
<th>Analysed region &amp; (method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese</td>
<td>F5</td>
<td>1.15</td>
<td>0.09</td>
<td>1.11</td>
<td>Allotriomorphic colony (SEM)</td>
</tr>
<tr>
<td>Chromium</td>
<td>F5</td>
<td>1.71</td>
<td>0.07</td>
<td>1.59</td>
<td>Acicular ferrite colony (SEM)</td>
</tr>
<tr>
<td>Silicon</td>
<td>F5</td>
<td>0.44</td>
<td>0.51</td>
<td>0.51</td>
<td>Colony (TEM)</td>
</tr>
<tr>
<td>Manganese</td>
<td>F6</td>
<td>1.24</td>
<td>0.13</td>
<td>1.11</td>
<td>Allotriomorphic colony (SEM)</td>
</tr>
<tr>
<td>Chromium</td>
<td>F6</td>
<td>1.74</td>
<td>0.14</td>
<td>1.59</td>
<td>Acicular ferrite colony (SEM)</td>
</tr>
<tr>
<td>Silicon</td>
<td>F6</td>
<td>0.54</td>
<td>0.08</td>
<td>0.51</td>
<td>Colony (TEM)</td>
</tr>
<tr>
<td>Manganese</td>
<td>F5</td>
<td>65.1</td>
<td>8.8</td>
<td>1.11</td>
<td>Inclusions (Carbon replica)</td>
</tr>
<tr>
<td>Chromium</td>
<td>F5</td>
<td>0.98</td>
<td>0.71</td>
<td>1.59</td>
<td>(TEM)</td>
</tr>
<tr>
<td>Silicon</td>
<td>F5</td>
<td>26.76</td>
<td>9.1</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>F5</td>
<td>5.4</td>
<td>5.0</td>
<td>0.009</td>
<td></td>
</tr>
</tbody>
</table>

4.3.2 Dilatometry

The variety of microstructures obtained with changing austenite grain size are shown in Figs. 4.8 and 4.9. As expected, those specimens austenitised at the higher temperature of 1150 °C for 10 minutes transformed into allotriomorphic ferrite and acicular ferrite, whereas the others, austenitised at 1000 °C for 10 minutes transformed predominantly into a classical bainitic microstructure with a very small amount of allotriomorphic ferrite. The important observation again is that the presence of substantial amounts of acicular ferrite was associated with that of austenite grain boundary allotriomorphic ferrite.

The isothermal transformation experiments described in Table 4.4 were analysed further by plotting the relative length changes recorded during transformation as a function of the transformation temperature. To allow for any reaction before to reaching \( T_i \), data at \( T_i \) were converted by linearly extrapolating the \( \Delta L/T \) temperature curve for the temperature range \( T_i \) to \( T_f \). This is shown schematically in Fig. 4.10; the actual curves are shown in Fig. 4.11. The length changes recorded at \( T_i \) and those estimated by extrapolation to \( T_i \) were analysed further to deduce the degree of reaction at \( T_i \) (Table 4.6). The calculations also enable the carbon
concentration in the residual austenite to be estimated, i.e., the experimental $z_\gamma$, which are marked on the calculated phase diagram shown in Fig. 4.12. The relative length change data obtained for all the dilatometric experiments indicate that some transformation could not be avoided before reaching $T_i$. As pointed out earlier, this is not important providing the total volume fraction of allotriomorphic ferrite is not very large.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$(\frac{\Delta L}{L})_{\text{max}}$</th>
<th>Volume fraction transformed</th>
<th>$x_\gamma$ (Experimental)</th>
<th>$T_i$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.0045</td>
<td>0.58</td>
<td>0.0053</td>
<td>505</td>
</tr>
<tr>
<td>S2</td>
<td>0.0042</td>
<td>0.54</td>
<td>0.0049</td>
<td>519</td>
</tr>
<tr>
<td>L1</td>
<td>0.0039</td>
<td>0.50</td>
<td>0.0045</td>
<td>513</td>
</tr>
<tr>
<td>L2</td>
<td>0.0035</td>
<td>0.45</td>
<td>0.0041</td>
<td>529</td>
</tr>
</tbody>
</table>

4.4 Discussion

It appears that, for the austenite grain size range studied here, the alloy used transforms into bainite (samples F3 and S1, S2) provided that the austenite grain boundaries are free to nucleate bainite. However, the transition from bainite to acicular ferrite can be stimulated by eliminating the austenite grain boundary nucleation sites (samples F4, F5 and L1, L2). The $\gamma/\gamma$ boundaries were destroyed in effect by the formation of thin layers of grain boundary allotriomorphic ferrite in both adjacent $\gamma$ grains. The transformation mechanisms for both acicular ferrite and bainite are also found to be similar, as confirmed by dilatometric experiments which gave results similar to those of Yang and Bhadeshia (1987a). The reaction clearly stopped at the point where $x_\gamma = x_{T_0}$.

The important new observation is connected with the effect of the prior phase transformation to allotriomorphic ferrite. For the present alloy, the overall hardenability is low compared with the alloys studied by Yang and Bhadeshia. Since, allotriomorphic ferrite was not observed in their experiments, the observed transition from bainite to acicular ferrite with increasing grain size could be attributed simply to the decrease in grain boundary sites for the nucleation of bainite; as it is well established, classical bainite nucleation starts at the $\gamma/\gamma$ grain boundaries (Bhadeshia, 1987a).
Thus, the present work gives an explanation of why high Cr welds tend to contain mostly bainite. Since the increase in Cr concentration reduces and eventually eliminates allotriomorphic ferrite, the austenite grain boundaries are free to nucleate the bainite before acicular ferrite can form intragranularly on the inclusions (Fig. 4.13).

Since both the acicular ferrite and bainitic ferrite reactions were found to terminate when \( x_{\gamma} \) reached \( x_{\gamma} \), the results confirm that the transformation mechanisms for bainitic ferrite and acicular ferrite are similar. Thin film carbon replica analysis failed to show any carbide precipitation in all the samples supporting the assumption inherent in equation (2.1). The experimentally measured carbon concentrations in the residual austenite at the point where the growth of acicular ferrite stopped, were found to be at somewhat lower carbon concentrations than estimated from the computed \( T_0 \) phase boundary (Fig. 4.12). This may be a consequence of a higher value of stored energy than that of 400 J mole\(^{-1}\) used in the present calculations.

The present results emphasise the fact the reactions taking place in the \( \gamma/\gamma \) grain boundaries can be crucial in determining the microstructures that develop in the weld metal. The ratio of the grain boundary and intragranular nucleation site densities can be modified to obtain the desired microstructure on transformation from austenite. The ability of inclusions to induce intragranular acicular ferrite is now a well established concept, though the nature and mechanism are not clear (Abson et al., 1978, Dowling et al., 1986, Ricks et al., 1981, 1982, Liu and Olson, 1986 and Bhadeshia, 1989). Removal of inclusions clearly causes an acicular ferrite microstructure to change to one which contains bainite (Harrison and Farrar, 1981). This is also apparent in the measured continuous cooling transformation diagrams published by Homma et al., (1987) which indicate that in the absence of oxide inclusions, austenite transforms into bainitic ferrite or Widmanstätten ferrite (Fig. 4.14). These two mechanisms are shown schematically in Fig. 4.13.

A search of the literature revealed that Cr and Mo are not the only elements to induce the formation of bainite at the expense of acicular ferrite. Similar effects can be deduced for manganese at high concentrations from the work by Horri et al., (1988) and Grong et al., (1986). In the latter work the "ferrite with aligned second phase" i.e., (Widmanstätten ferrite or bainite) content was found to decrease with increase in Mn, as the acicular ferrite content increased. However, after an optimum level of manganese, the acicular ferrite began to be replaced to increasing degrees by "ferrite with aligned second phase", as the volume fraction of grain boundary allotriomorphic ferrite also decreased.

It remains to be explained why the layers of allotriomorphic ferrite themselves appear incapable of nucleating bainite. The reason could be associated with the fact that the \( \alpha/\gamma \) interface may not be stationary at the temperature \( T_2 \). However, this is an unlikely explanation since
the reconstructive transformation of austenite to allotriomorphic ferrite is extremely sluggish at the temperatures where bainite forms. The alternative explanation is that the solute field, owing to elements displaced by the $\alpha$ into the adjacent $\gamma$, prevents the nucleation of bainite. If we consider the growth of allotriomorphic ferrite to occur by a paraequilibrium mechanism, then only the carbon composition profile ahead of the interface needs to be considered. With this assumption, consistent with the microanalysis data, allotriomorphic ferrite growth can be considered to be controlled by diffusion of carbon in the austenite ahead of the interface. The carbon composition profile in front of the moving interface can be calculated for various temperatures using the following equation (Coates, 1973b).

$$z(X, t) = \bar{z} + [z^{7\alpha} - \bar{z}] E_1\{X, D\}$$  \hspace{1cm} (4.3)

where

$$E_1\{X, D\} = \left[\frac{1 - erf\left(\frac{X}{4Dt^{0.5}}\right)}{1 - erf\left(\frac{Z}{4Dt^{0.5}}\right)}\right]$$  \hspace{1cm} (4.4)

where $X$ is the distance ahead of the the moving $\alpha/\gamma$ interface, $Z$ is the thickness of the allotriomorphic ferrite grown after a time $t$ from the initiation of growth, and $D$ is the weighted average diffusivity of carbon in austenite given by Trivedi and Pound (1967).

The thickness of the allotriomorphic ferrite can be predicted using the equation (4.2). Since the growth took place while cooling, the value of $Z$ and also of other variables should correspond to a condition where the allotriomorphic ferrite growth ceases. To simplify the problem the theoretical analysis was carried out for two cases: (i) the static case in which on cooling from $T_1$ to $T_2$, the carbon composition profile in the austenite does not change at $T_2$ and (ii) the dynamic case when the carbon tries to diffuse from a carbon enriched sessile $\alpha/\gamma$ interface to a more homogeneous composition throughout the residual austenite.

4.4.1 Static case

It is possible that the region of carbon enriched austenite in the vicinity of the allotriomorphic ferrite/austenite interface suppresses the nucleation of bainite at that interface. As the allotriomorphic ferrite formation temperature decreases, $z^{7\alpha}$ increases and the $W_S$, $B_S$ and $M_S$ temperatures of austenite of composition $z^{7\alpha}$ decrease, as illustrated in Fig. 4.15b. The transformation temperatures were all calculated according to Bhadeshia (1981a, 1982a). If the isothermal transformation temperature $T_2$ is above the calculated $W_S$ or $B_S$ temperatures for the austenite at the $\alpha/\gamma$ interface, then it can be concluded that the interface is incapable of nucleating Widmanstätten ferrite or bainite. Such a situation arises for all temperatures below the point marked ‘A’ ($\approx 720 \degree C$) on Fig. 4.15b. Since $T_2$ was in the present case always below 720 °C, the calculations are consistent with the result that no Widmanstätten ferrite or bainite
could be observed to nucleate from $\alpha/\gamma$ interfaces, thus making the allotriomorphic ferrite ideal for the purpose of stimulating the intragranular growth of $\alpha_a$.

4.4.8 Dynamic case

This above model may not be valid if the carbon concentration profile at the $\alpha/\gamma$ interface homogenises during heat treatment at $T_2$. The growth of allotriomorphic ferrite becomes very sluggish indeed at temperatures below $B_S$ and it is assumed here that it actually stops, thereby providing opportunity for homogenisation. A finite difference method (see Appendix) was used to test whether the carbon concentration profile, which develops during the growth of allotriomorphic ferrite at $T_1$, changes sufficiently on holding at $T_2$, to enable the austenite in the vicinity of the $\alpha/\gamma$ interface to decompose to bainite. The initial composition profile was established using equation (4.3) and assuming the allotriomorphic ferrite thickness is about 5 $\mu$m.

The calculations are carried out for $T_1 = T_C$, where $T_C$ is the temperature where the upper and lower ‘C’ curves of the TTT diagram intersect. At $T_C$, displacive reactions become kinetically favoured after reconstructive transformations, so that $T_C$ can be assumed to be the temperature at which the allotriomorphic ferrite growth stops. The homogenisation of carbon on subsequent treatment at $T_2 = 470 ^\circ$C is illustrated in Figs. 4.16 and 4.17. Even after holding for 120 seconds at $T_2$ (the longest reaction time used in the experiments), the calculations proved that the carbon content in the enriched austenite at the $\alpha/\gamma$ interface remains high enough to prevent the formation of bainite.

It is of interest to examine other possible methods for rendering the austenite grain surfaces ineffective as possible bainite nucleation sites. The work of Mori et al., (1980) Snieder and Kerr (1984) and Fleck et al., (1986) in which boron is used as an alloy addition is relevant this respect. Finally, it should be noted that it may not be necessary to completely cover the austenite grain boundaries with allotriomorphic ferrite, since the ferrite will nucleate first at the most potent sites, thus eliminating them for the purpose of bainite nucleation. It is also relevant to point out that fewer than half of the allotriomorphic ferrite are likely to be in a crystallographic orientation suitable to stimulate $\alpha_W$ or $\alpha_b$ growth even if the enriched austenite of $\gamma$ at the $\alpha/\gamma$ interface did not prevent such growth. The reported increase in the acicular ferrite by Snieder and Kerr (1984) using boron additions implies that the procedure could be considered for stimulating acicular ferrite in Fe-Cr-Mo-C welds also.

4.5 Conclusions

It is found that in weld metals containing inclusions the transition from bainite to acicular ferrite can be stimulated by the prior formation of a small amount of allotriomorphic ferrite
along the austenite grain surfaces. This could be one of the main reasons why Fe-Cr-Mo-C welds tend to have predominantly bainitic microstructures at high alloy concentrations, since the allotriomorphic ferrite formation is then suppressed. Providing that the austenite grain boundaries are free to nucleate bainitic ferrite, the latter phase, in general cannot be avoided and its formation will lead to a corresponding reduction in the quantity of acicular ferrite. It is probable that any allotriomorphic ferrite which is in a suitable orientation relationship to stimulate bainite cannot in fact do so, because the solute concentration in the enriched austenite at the allotriomorphic ferrite/austenite interface prevents it from transforming to bainite. This hypothesis has been confirmed using finite difference analysis which indicated that the time taken for the carbon to homogenise is much higher than that required for $\alpha_n$ formation.
APPENDIX

Finite difference method

The carbon composition profile build up ahead of the allotriomorphic ferrite / austenite interface in the residual austenite, is examined here using a finite difference method to simulate any homogenisation of concentration. The main advantage of the application of finite difference method to this problem is that it can handle the changing boundary conditions during the homogenisation process. The finite difference method is based on the technique discussed by Crank (1975). The model assumes a one dimensional diffusion process ahead of a planar allotriomorphic - austenite interface. The initial profile set up at a time $t = 0$, is given by the analytical equation as discussed in the main text. The composition profile is then subjected to finite difference method after normalising the variables to dimensionless quantities suitable for this method. The normalised variables are as follows

$$
Distance \; X = \frac{x}{(\frac{x_i}{2} - q)}
$$

$$
Concentration \; C = \frac{C_{i,j}}{C^{\gamma\alpha}}
$$

$$
Time \; T = \frac{D t}{x^2}
$$

where $x$ is the distance from the $\alpha/\gamma$ interface, $q$ is the half thickness of ferrite and $\gamma_{g.a}$ is the austenite grain size. $C_{i,j}$ is the composition at any time step $j$ and at position $i$ from the interface and $C^{\gamma\alpha}$ is the composition of interface at $t = 0$. $D$ is the average diffusivity calculated for every time step $\delta t$. Here the interface position does not move with time, since allotriomorphic ferrite growth is assumed to be completed. The interface composition is determined for each time step by the mass balance. The area under the normalised composition profile is calculated using numerical integration. The general finite difference equation for the composition in the next time interval is

$$
C^\gamma_{i,j+1} = C^\gamma_{i,j} + R(C^\gamma_{i-1,j} - 2C^\gamma_{i,j} + C^\gamma_{i+1,j})
$$

where $R = D\delta t/(\delta x)^2$, and is taken to be 0.1. This particular value was assumed after checking that variation of $R$ coefficient from 0.1 - 0.3 made negligible difference to the results. $C^\gamma_{i,j+1}$ is the composition at $i$ position of interface and at a time step $j + 1$ and is derived from the compositions at the $i − 1, i, i + 1$ positions at a time step of $j$. The diffusivity for next time step is calculated from the composition profile for the current time. The flow chart for the program is presented in Fig. 4.18.

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Fig. 4.1 Calculated (a) phase diagram and (b) TTT diagram based on the model developed by Bhadeshia (1981a, 1982a) for Fe - 0.053C - 0.51Si - 1.11Mn - 1.59Cr (wt.%) weld metal.
Fig. 4.2 Schematic illustration of the furnace heat treatments: The path ABD shows a two step heat treatment, and ACD a single step heat treatment, respectively; Three resistance heated furnaces were used.
Fig. 4.3 Typical data used for measurement of (a) austenite and (b) ferrite linear thermal expansion coefficients. The correlation coefficient of the data were found to be more than 0.99, when subjected to linear regression analysis.
Fig. 4.4 Lattice parameter measurement by extrapolation of Nelson-Riley function (see section 2.4): points represent the lattice parameter measured from the angles measured from various sets of planes; solid line is the fitted line with weighting; and the intercept at Y axis for Nelson-Riley function value of zero gives the lattice parameter of ferrite.
Fig. 4.5 Microstructures obtained in the furnace experiments F3-5.

a. F3; Microstructure depicting bainitic sheaf structure (microhardness measured was 278 HV).

b. F4; Microstructure of acicular ferrite and grain boundary allotriomorphic ferrite (microhardness of acicular ferrite region was 285 HV).
Fig. 4.5 continued....

c. F5; Microstructure of allotriomorphic ferrite and acicular ferrite; note that the thickness of allotriomorphic ferrite is bigger than F4 (microhardness measured in the acicular ferrite region was 283 HV).
Fig. 4.5 continued....

d. F3; Bright field image illustrating the sheaf structure of bainite (inset is the diffraction pattern from a <001> ferrite zone axis)

e. F3; Corresponding dark field image using (020) spot, showing that the bainitic platelets within the sheaf are all in the same crystallographic orientation.
f. F5; microstructure indicating possible acicular ferrite nucleation away from the $\alpha/\gamma$ interface (dark phase could be martensite transformed from carbon enriched austenite).
Fig. 4.6 Microstructures obtained in the furnace experiments F6-8.

a. F6; Microstructure on transformation by continuous cooling (note the similarity between this microstructure and the typical weld microstructures that develop in ordinary C-Mn weld metals).
Fig. 4.6 continued....

b. F6; Typical microstructure developed near to $\alpha/\gamma$ interface. The microstructure depicts the allotriomorphic ferrite and acicular ferrite colony away from the interface. The dark phase could be martensite formed from the carbon enriched austenite.
c. F7; Microstructure developed by transformation above $B_S$, $T_2=600 \, ^\circ C$ after $T_1=800 \, ^\circ C$; the microstructure is essentially allotriomorphic ferrite and martensite.

d. F8; The residual austenite islands transformed to martensite by quenching after $T_1=800 \, ^\circ C$; proving the fact that the acicular ferrite morphology develops only by transformation below $B_S$. The hardness measured in the martensitic region was found to be 352 HV and that of allotriomorphic ferrite was found to be 193 HV.
Fig. 4.7 Details of EDX analysis on samples from furnace experiments.

a. Region analysed by EDX in TEM, in the sample F6, across an allotriomorphic ferrite and an acicular ferrite colony. The line represents the region over which the analysis were carried out.

b. Variation of Si, Mn and Cr as measured by the EDX analysis over a line as shown in the Fig. 4.7a. The first 10 points correspond to the allotriomorphic ferrite region and the rest to acicular ferrite colony. The variation shows no systematic change in alloying element concentration.

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c. The allotriomorphic ferrite and acicular ferrite microstructure as observed in SEM, which was subjected to EDX analysis.

d. Variation of Si, Mn and Cr as measured by EDX analysis over the spots as shown in the Fig. 4.7c. The points 1-6 correspond to the analysis obtained from allotriomorphic ferrite region and rest from the acicular ferrite region.
Fig. 4.8 The comparison microstructure of isothermally transformed samples from dilatometric experiments.

a. L1: Illustrating the effect of allotriomorphic ferrite on promoting acicular ferrite

b. S1: Microstructure of predominantly bainite; no grain boundary allotriomorphic ferrite can be seen.
Fig. 4.9 Transmission electron micrographs of isothermally transformed samples in dilatometric experiments:

a. L1: Typical acicular ferrite plates nucleating from inclusion and also the impingement of that plate with nearby plates also could be observed.

b. S1: Bainitic sheaf structure nucleating from prior $\gamma/\gamma$ interface. Inclusions are also seen along the grain boundary.
Fig. 4.10 Schematic diagram illustrating the extrapolation method to calculate the maximum relative length change at isothermal heat treatment temperature \( (T_i) \); given a case where there is transformation before reaching the temperature \( T_i \) while cooling from austenite phase field. The dark line indicates the actual relative length change.
Fig. 4.11 Comparison of $\Delta L/L$: temperature plots for the dilatometric experiments as mentioned in Table 4.4. The plots show the transformation start temperature and extrapolation procedure for calculating the maximum length change at $T_s$.

a. L1 and L2; After $T_S$, the transformation rate seem to be very high as indicated by its rate of slope change of actual $\Delta L/L$. Temperature curve from extrapolated straight line. This indicates the allotriomorphic ferrite transformation while cooling from $T_s$. This is also supported by high $\Delta t_{850-T_s}$ (Table 4.3).
Fig. 4.11 continued....

b. S1 and S2: Though the transformation started at very high temperature, as seen in the graph, because of less $\Delta t_{550-T_1}$ (Table 4.3), the transformation to allotriomorphic ferrite was comparatively less. This can be reasoned from the rate of slope change of actual $\Delta L$. Temperature curve with respect to extrapolated straight line.
Fig. 4.12 Comparison of experimental $x_p$ points corresponding to maximum volume fraction of ferrite for the dilatometer experiments and the phase boundary line calculated by Bhadeshia (1981a, 1982a). L represents high $T_\gamma$ specimens and S represents low $T_\gamma$ specimens.
Transition from Bainite to Acicular ferrite

Fig. 4.13 Schematic illustration of mechanisms of transition from acicular ferrite to bainite due to the published ones and also due to the present results (see next page).

a. Effect of varying inclusion density for the same austenite grain size.
b. Effect of varying austenite grain boundary nucleation site density (grain size effect)
c. Effect of prior transformation to allotriomorphic ferrite for the same austenite grain size.
Fig. 4.14 Comparison CCT diagram for the weld metal containing $Ti_2O_3$ and no $Ti_2O_3$, after Homma et al., (1987). The region B represents bainite and AF represents acicular ferrite. The presence of $Ti_2O_3$ promotes the formation of acicular ferrite.
Fig. 4.15 The diagrams illustrate the condition for nucleation of bainite at the allotriomorphic ferrite/austenite interface. The upper graph is essentially a representation of the $Ae_3$ phase boundary line for the present alloy. If the second isothermal transformation temperature is higher than the calculated $W_S$ or $B_S$ temperatures then the nucleation of Widmanstätten ferrite or bainite is impossible. The point A represents the lowest allotriomorphic ferrite transformation temperature below which the $\alpha/\gamma$ interface is found not to be capable of nucleating Widmanstätten ferrite or bainite.

a. Variation in $x^{\gamma\alpha}$ as a function of the temperature at which allotriomorphic ferrite grows.

b. Variation in $W_S$, $B_S$, and $M_S$ temperatures of the austenite at the allotriomorphic ferrite/austenite interface, as a function of the transformation temperature at which the allotriomorphic ferrite grows by paraequilibrium transformation.
Fig. 4.16 The cascade of carbon composition profile for a time duration of 120 seconds at $T_2=470$ °C. The graph was drawn by normalising interface composition with respect to initial interface composition and the distance by half value of $\gamma'_{\text{res}}$ (residual austenite grain size). The initial profile set up was calculated as discussed in the text for a transformation temperature of 600 °C. The figure shows that in the time period at $T_2$ the carbon composition neither gets homogenised nor reduces to certain level that point A could be reached as explained in static case. (This analysis assumes there is no change in the interface composition as it cools to $T_2$).
Fig. 4.17 The cascade of interface composition only with respect to time at $T_2=470$ °C. The interface composition only drops to 0.358 wt.% which is still less than the point A for the condition for nucleation of bainite at allotriomorphic - austenite interface. Before this could be achieved the intragranular inclusions could stimulate the formation of acicular ferrite.
Fig. 4.18 Flow Chart indicating the finite difference method for simulating the cascade of interface composition with time.
Chapter 5

Mechanism of the Transition from Bainite to Acicular Ferrite

5.1 Introduction

Acicular ferrite is also found in wrought steels which have deliberately been inoculated with nonmetallic inclusions (Imagumbai et al., 1985, Yamamoto et al., 1987, Nishioka et al., 1988). Present and previous experimental data have provided convincing evidence that acicular ferrite is essentially intragranularly nucleated bainite (Yang and Bhadeshia 1987a, Strangwood and Bhadeshia, 1987a, Sugden and Bhadeshia, 1989b). Some of the experimental results which confirm that acicular ferrite is nothing but intragranularly nucleated bainite were summarised schematically in Fig. 4.13. The transformation temperatures are identical for all the cases illustrated, the differences being that: (Fig. 4.13a) inclusion density changed for the same austenite grain size (Harrison and Farrar, 1981); (Fig. 4.13b) an increase in the austenite grain size at constant inclusion density stimulates a transition from a predominantly bainitic to an acicular ferrite microstructure (Yang and Bhadeshia, 1987a); (Fig. 4.13c) the growth of a layer of inert allotriomorphic ferrite at the austenite grain surfaces causes a transition from bainite to acicular ferrite (chapter 4). Henceforth, active allotriomorphic ferrite is defined as that which is able to develop into other transformation products such as Widmanstätten ferrite or bainite at the transformation temperature of interest. The allotriomorphic ferrite is said to be inert when the local reduction in transformation temperature at the ferrite/austenite interface due to the partitioning of carbon prevents the development of secondary Widmanstätten ferrite or bainite. The present chapter describes experiments to investigate this mechanism.

5.2 Method & Experimental Techniques

To enable the acicular ferrite/bainite transition to be studied easily, it is necessary that the steel used should contain a substantial quantity of nonmetallic inclusions of the type responsible for the nucleation of acicular ferrite. Consequently, steel samples machined from alloy 77 were used in this study. The composition is presented in Table 2.2. The sample preparation procedures were similar to the method described in chapter 2. Subsequent heat–treatments were conducted in a Theta Industries high-speed dilatometer with a helium gas–quench facility. The austenitisation treatment was carried out under helium in the dilatometer chamber. The prior austenite grain size generated by austenitising at 1150°C for 10 minutes was found to be about 70 μm (mean lineal intercept). Regular optical and transmission electron micrography was carried out.
Details of the dilatometric technique have been described previously; the interpretation of such data requires a knowledge of lattice parameters and thermal expansivities of the phases involved. The lattice parameter of ferrite was measured using X-ray diffraction (Debye–Scherrer, Cu–K\textsubscript{α}, 45 kV). With a Nelson–Riley extrapolation of the measured data, the accurate ferrite lattice parameter was found to be 0.28739 ± 0.00024 nm. For austenite, the lattice parameter can be estimated using published data (Dyson and Holmes, 1970 and Bhadeshia, 1982b). The thermal expansion coefficients of austenite and ferrite were measured dilatometrically to be $1.9955 \times 10^{-5} \pm 0.2 \times 10^{-7}$ K\textsuperscript{-1} and $1.3941 \times 10^{-5} \pm 0.2 \times 10^{-7}$ K\textsuperscript{-1} respectively.

5.3 Results & Discussion

5.3.1 Heat–Treatment

Figure 5.1 illustrates the calculated time–temperature–transformation (TTT) diagram for the alloy using the procedures developed by Bhadeshia (1982a). If thin layers of allotriomorphic ferrite (α) are to be utilised in order to prevent austenite (γ) grain boundary nucleated reactions from stifling the development of intragranularly nucleated acicular ferrite, then the allotriomorphic ferrite itself must be inert. It is well known, however, that Widmanstätten ferrite packets or bainite sheaves are often seen to grow from α/γ interfaces, especially when the α has an orientation with the austenite which is in the Bain region (Crosky et al., 1980). In other circumstances, the ferrite appears unable to develop into other transformation products (chapter 4). A major purpose of this work was to investigate whether it is the carbon diffusion field established at a temperature $T_\alpha$ in front of the allotriomorphic ferrite/austenite interface that sometimes prevents the ferrite from developing into Widmanstätten ferrite or bainite during subsequent transformation at a lower temperature $T_b$.

A series of experiments was designed to investigate the role of the partitioned carbon (Fig. 5.2, Table 5.1); the detailed choice of transformation temperatures for these experiments is discussed later:

(a) Heat–treatment H1 involved a low allotriomorphic ferrite transformation temperature ($T_\alpha$), in order to render it inert (a low $T_\alpha$ corresponds to a large value of $z^\circ$, the carbon concentration in the austenite at the austenite/ferrite interface).

(b) As a control experiment, H2 was designed with a high $T_\alpha$, such that the allotriomorphic ferrite would be active on subsequent transformation at $T_b$.

(c) Any carbon build up at the α/γ interface can in principle be homogenised by annealing at a high temperature $T_\alpha > T_\alpha$. This could render initially inert allotriomorphic ferrite active. Heat–treatments H3 and H4 were designed to test this idea.

(d) In heat–treatment H5, the temperature $T_b$ was deliberately set to be larger than the
bainite–start temperature of the alloy, in order to confirm that acicular ferrite, which is supposed to be intragranularly nucleated bainite, does not form.

Table 5.1 Heat–treatment schedules. The samples were austenitised at 1150 °C for 10 minutes prior to transformation at lower temperatures. The temperatures (T) are all stated in °C, and the corresponding time periods (t) in minutes. The samples were all quenched after the final isothermal reaction. T_α is the allotriomorphic ferrite growth temperature, T_α is an annealing temperature and T_b is a bainitic transformation temperature.

<table>
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<tr>
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<th>T_α</th>
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<th>t_α</th>
<th>T_b</th>
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<td>H1</td>
<td>660</td>
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<td>-</td>
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<tr>
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</tr>
<tr>
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<td>750</td>
<td>1.0</td>
<td>500</td>
<td>60</td>
</tr>
<tr>
<td>H5</td>
<td>660</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>600</td>
<td>1</td>
</tr>
</tbody>
</table>

The temperatures for the heat–treatments just described were determined theoretically, by calculating the Widmanstätten ferrite–start and bainite–start temperatures for the austenite (of composition x^γ) adjacent to the allotriomorphic ferrite, as illustrated in Fig. 5.3. In Fig. 5.3, the horizontal axis represents the temperature at which allotriomorphic ferrite grows, whereas the vertical axis represents the Widmanstätten ferrite–start or bainite–start temperature of the austenite at the allotriomorphic ferrite/austenite interface. The method for thermodynamic and transformation–start calculations have been described before (chapter 1). It is clear from Fig. 5.3 that for T_α = 660°C, the allotriomorphic ferrite is expected to be inert when T_b = 500°C. For the same value of T_b = 500°C, allotriomorphic ferrite generated by transformation at T_α > 720°C is expected to be active.

These calculations are valid for heat–treatments H1 and H2, which do not include any intermediate annealing treatment at T_α. They assume therefore that any carbon concentration built up in the austenite as the allotriomorph grows, is retained as the sample is cooled rapidly to T_b. On the other hand, samples H3 & H4 were annealed at T_α immediately after the growth of allotriomorphic ferrite and before heat–treatment at T_b. It is therefore necessary to model any change in the carbon concentration profile ahead of the α/γ interface during the annealing treatment.

The distribution of carbon (x) in front of a ferrite allotriomorph of half–thickness Z in the absence of soft–impingement is given by Coates (1973b).
\[ x(X, t) = \bar{X} + (\bar{Z} - \bar{X}) \left[ \frac{1 - \text{erf} \left( X/(4Dt)^{0.5} \right)}{1 - \text{erf} \left( Z/(4Dt)^{0.5} \right)} \right] \]  

(5.1)

where \( X \) is the distance in the austenite ahead of the interface, and \( \bar{X} \) is the average carbon concentration of the steel. \( D \) is the weighted average carbon diffusivity in austenite (Trivedi and Pound, 1967):

\[ D = \int_{\bar{Z}}^{\bar{Z}} D(x)/(\bar{X} - x^{0.5}) \]  

(5.2)

where \( D \) is the concentration dependent diffusion coefficient of carbon in austenite, calculated as in Siller and Mclellan (1969, 1970).

Having calculated this carbon concentration profile generated at \( T_\alpha \), a finite difference method described in chapter 4 was utilised to see how it homogenises during heat–treatment at \( T_\alpha \) (Fig. 5.4). The concentration at the ferrite/austenite boundary after the annealing treatment is therefore known, permitting the calculation of Widmanstätten ferrite–start and bainite–start temperatures at that location. With the help of such calculations, it was possible to demonstrate (Table 5.2) that heat–treatments H3 and H4, both of which incorporate an intermediate anneal at \( T_\alpha \), should activate the ferrite which would otherwise be inert. The ferrite half–thickness values necessary for the calculations were measured directly using optical microscopy to be around 3.5 \( \mu \)m. This probably overestimates the thickness due to sectioning errors. The calculations nevertheless demonstrated that even with any overestimated thickness, the annealing treatment is more than adequate in activating the ferrite.

Fig. 5.5 shows the microstructure of a sample which was quenched directly from the austenitisation temperature to another temperature (500 °C) below \( B_S \). The experiment confirms that in ordinary circumstances, heterogeneous nucleation at the austenite grain surfaces dominates the transformation behaviour, leading to a fully bainitic microstructure rather than one containing intragranularly nucleated bainite (i.e., acicular ferrite). This is in complete contrast with the microstructure obtained during heat–treatment H1 (Fig. 5.6), in which the first transformation product to form is allotriomorphic ferrite, which completely decorates the austenite grain surfaces. Since this allotriomorphic ferrite is inert (Table 5.2), transformation at \( T_\alpha \) leads to the formation of acicular ferrite.

Figure 5.7 (heat–treatment H2) shows a case where the allotriomorphic ferrite is ineffective. Because it formed at a relatively higher temperature, \( x^{0.5} \) is small enough to permit the ferrite to develop into bainite during transformation at \( T_\alpha \). There is clear evidence of the growth of bainite sheaves from the allotriomorphic ferrite (which is therefore classified to be active, Table 5.2); consistent with theory, bainite is obtained instead of acicular ferrite.
Table 5.2 The results of calculations designed to indicate whether the allotropic ferrite generated in heat-treatments H1–H4 should be inert or active. \( x^{2\alpha}_{T_\alpha} \) is the carbon concentration in the austenite at the \( \alpha/\gamma \) interface at the temperature \( T_\alpha \). \( x^{2\alpha}_{T_\alpha} \) is the carbon concentration in the austenite at the \( \alpha/\gamma \) after heat-treatment at \( T_\alpha \). Since \( T_\beta = 500^\circ C \), \( x^{2\alpha}_{T_\alpha} \) must be less than 0.011 mole fraction if the ferrite is to be active during isothermal holding at \( T_\beta \). The microstructure observed experimentally (within the austenite grains) is listed in the last column. The concentrations are all in mole fractions, the temperatures in °C and time in minutes.

<table>
<thead>
<tr>
<th></th>
<th>( T_\alpha )</th>
<th>( t_\alpha )</th>
<th>( x^{2\alpha}<em>{T</em>\alpha} )</th>
<th>( T_\alpha )</th>
<th>( t_\alpha )</th>
<th>( x^{2\alpha}<em>{T</em>\alpha} )</th>
<th>microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>660</td>
<td>1</td>
<td>0.0274</td>
<td>501</td>
<td>5</td>
<td>0.0224</td>
<td>acicular</td>
</tr>
<tr>
<td>H2</td>
<td>740</td>
<td>4</td>
<td>0.0086</td>
<td>500</td>
<td>60</td>
<td>0.0079</td>
<td>bainite</td>
</tr>
<tr>
<td>H3</td>
<td>660</td>
<td>1</td>
<td>0.0274</td>
<td>760</td>
<td>0.5</td>
<td>0.0119</td>
<td>bainite</td>
</tr>
<tr>
<td>H4</td>
<td>660</td>
<td>1</td>
<td>0.0274</td>
<td>750</td>
<td>1.0</td>
<td>0.0092</td>
<td>bainite</td>
</tr>
</tbody>
</table>

Experiments H3 and H4 both show bainitic microstructures (Fig. 5.8a,b), because in both cases, the annealing treatment at \( T_\alpha \) leads to a reduction in the concentration of carbon at the \( \alpha/\gamma \) interface, rendering the allotropic ferrite active.

Fig. 5.9 confirms that acicular ferrite will not form if \( T_\beta \) is greater than the bainite–start temperature of the alloy, even when the austenite grain boundaries are covered with layers of inert allotropic ferrite. Heat-treatment H5 has a microstructure of just allotropic ferrite and the martensite obtained on quenching to ambient temperature.

5.3.2 Interpretation of dilatometric data

The dilatometric technique can be extremely useful in studying transformations because it allows the transformation to be followed as it happens (Fig. 5.10). The three typical examples presented in Fig. 5.10 illustrate direct transformation to bainite, a two-stage heat-treatment involving first the formation of allotropic ferrite and then acicular ferrite, and finally, a three-stage heat-treatment in which the sample is annealed at an elevated temperature after the growth of allotropic ferrite. It is particularly notable that in the latter case, no transformation occurs during annealing at \( T_\alpha \), although the distribution of carbon must homogenise as discussed earlier. This is because the paraequilibrium fraction of ferrite at \( T_\alpha \) is approximately that which was induced to form at \( T_\alpha \).

Figure 5.11a illustrates the length change observed during isothermal transformation at 660°C; the incubation time prior to the onset of substantial reaction is about 10 s, which is
consistent with the calculated TTT diagram presented in Fig. 5.1. Fig. 5.11b shows the how the isothermal transformation at temperatures below $T_S$ ceases, so that the carbon concentration of the residual austenite at that stage can be compared against the $T_0'$ curve (discussed later) in order to deduce the mechanism of transformation.

The dilatometric data can be interpreted further, since the length changes can be converted into the volume fraction of transformation using the lattice parameter and thermal expansivity measurements presented earlier (Bhadeshia, 1982b, chapter 2 and 4). The volume fraction data can in turn be combined with a conservation of mass criterion to estimate the carbon concentration of the residual austenite at any stage of reaction. It is interesting to see that for heat–treatments H1 and H4, the formation of acicular ferrite and bainite (respectively) ceases as the carbon concentration of the residual austenite reaches the $T_0'$ curve of the phase diagram (Fig. 5.12). This curve defines the locus of all points on the phase diagram at which austenite and strained–ferrite of the same composition have the same free energy (see for example, Bhadeshia and Christian, 1990). If that carbon concentration is exceeded, then transformation cannot proceed without the partitioning of carbon. Bainite and acicular ferrite are both known to stop growing when the $T_0'$ curve is reached, indicating the existence of an *incomplete reaction phenomenon* which can be interpreted to indicate that bainite and acicular ferrite grow without diffusion, any partitioning of carbon occurring after the growth event. These results are therefore significant in two respects; firstly, acicular ferrite is once again confirmed to have the same mechanism of transformation as bainite, in agreement with previous results. The second point is that the enrichment of austenite caused by the initial partial transformation to allotriomorphic ferrite also contributes to an early cessation of transformation to bainite or acicular ferrite.

5.4 Conclusions

The formation of acicular ferrite in steels containing intragranular nucleation sites can be enhanced by reducing the number density of austenite grain boundary nucleation sites. This can be done by decorating the austenite grain surfaces with thin layers allotriomorphic ferrite. The ferrite must however, be inert in the sense that it should not develop at lower transformation temperatures into secondary Widmanstätten ferrite or bainite. It can be rendered inert by the the partitioning of carbon into the austenite at the ferrite/austenite interface, as long as the local concentration is large enough to depress the local Widmanstätten ferrite–start or bainite–start temperature below the actual heat–treatment temperature. Finally, the results are all consistent with the hypothesis that acicular ferrite is nothing but intragranularly nucleated bainite.
Fig. 5.1 Calculated time–temperature–transformation diagram for the alloy studied. The thermodynamically calculated transformation temperatures (°C) are $M_s = 427$, $B_s = 546$, $W_s = 680$, $Ae_3 = 760$ and $Ae_3' = 828$ representing the martensite–start, bainite–start, Widmanstätten ferrite–start, paraequilibrium $\gamma/(\gamma + \alpha)$ temperature and equilibrium $\gamma/(\gamma + \alpha)$ temperature respectively.
Fig. 5.2 Schematic illustration of the heat-treatments used.
Fig. 5.3 Calculations designed to predict whether the allotriomorphic ferrite should be inert or active. (a) Variation of $\gamma^\circ$ as a function of the temperature at which allotriomorphic ferrite grows. (b) The horizontal axis represents the temperature at which allotriomorphic ferrite is induced to form. The vertical axis represents the Widmanstätten ferrite—start or bainite—start temperature of the austenite at the allotriomorphic ferrite/austenite interface.
Fig. 5.4 Finite-difference modelling of the homogenisation of the carbon concentration profile generated during the growth of allotriomorphic ferrite. The figure shows variation of $z^{700}$ as a function of time at a given ageing temperature $T_a$. Notice that the ageing heat-treatment at 500 °C (the temperature at which bainite or acicular ferrite are formed) hardly reduces the $z^{700}$, in comparison to heat-treatment at 760 °C.
Fig. 5.5 The bainitic microstructure generated during isothermal transformation at 500 °C for 60 minutes followed by quenching to ambient temperature.

Fig. 5.6 The microstructure generated by heat-treatment H1. The allotriomorphic ferrite layer is inert, giving acicular ferrite in the interiors of the austenite grains.
Fig. 5.7 The microstructure generated by heat-treatment H2, in which the allotriomorphic ferrite is active, with bainite sheaves in the middle of the austenite grains:

(a) optical micrograph,
(b) thin foil transmission electron micrograph of allotriomorphic ferrite and bainite sheaf.
Fig. 5.8 The microstructures generated by heat-treatments H3 (a) and H4 (b), where the allotriomorphic ferrite was activated by annealing at 750 and 750 °C, respectively. Bainite sheaves have formed as a consequence.
Fig. 5.9 The microstructure generated by heat-treatment H3, consisting of allotriomorphic ferrite and martensite, since isothermal holding at a temperature above $B_s$ did not cause any transformation.
Fig. 5.10 Dilatometric data: (a) direct transformation below the bainite–start temperature; (b) two-stage heat-treatment in which the initial transformation to allotriomorphic ferrite is followed by further transformation below $B_S$; (c) as in (b), but with an elevated temperature anneal imposed between the allotriomorphic and bainitic transformation to homogenise carbon in the residual austenite (see overleaf).
Fig. 5.11 (a) Dilatometric data showing that substantial transformation begins after about 10 s at 660 °C, consistent with the calculated TTT diagram of Figure 5.1. (b) Illustration of the fact that isothermal transformation within the bainite temperature range leads to a fairly rapid cessation of reaction, permitting the carbon concentration of residual austenite at that stage to be compared against the $T_o'$ phase boundary.
Fig. 5.12 The carbon concentrations of the austenite that is left untransformed after the cessation of the acicular ferrite or bainitic transformation (in a mixed microstructure which also contains some allotriomorphic ferrite), plotted together with calculated phase boundaries. The transformations clearly cease well before the austenite reaches its paraequilibrium or equilibrium composition.
Chapter 6

Continuous Cooling Transformation Characteristics of Fe-Cr-C Reheated Weld Metals

6.1 Introduction

The work so far explains the transition from acicular ferrite to bainite, in the case of Fe-Cr-C weld metals (see chapter 4) and indeed is consistent with other published results of Horri et al., (1988), Grong et al., (1986) and Harrison and Farrar (1987a,b). Thus, acicular ferrite can be encouraged by introducing a controlled layer of allotriomorphic ferrite all along the austenite grain boundaries. This chapter is a first step towards the application of these concepts to practical weld situations.

Some published data suggest that the acicular ferrite plate size, in a mixed microstructure of $\alpha_a$ and $\alpha_s$, is a function of the austenite grain size (Dallam and Olson, 1989, Fleck et al., 1986). Coarser austenite grains lead to finer plates and vice versa. It also appears that a sample with finer acicular ferrite showed better toughness characteristics. An explanation for these observations is as follows: the ratio of the allotriomorphic ferrite thickness to austenite grain size changes ($q_a/R_s$) is a function of the volume fraction of ferrite. Allotriomorphic ferrite growth involves the partitioning of solutes. In the case of welds, transformation proceeds mainly by a paraequilibrium mechanism, so that the solute partitioning is carbon. Dallam and Olson assumed that the partitioned carbon is uniformly distributed in the residual austenite, which will then have a reduced free energy for transformation to ferrite. This stabilisation of the austenite by carbon enrichment may somehow lead to different transformation kinetics and hence different plate size.

This assumption of a homogeneous residual austenite is not justified from the work presented in chapters 4 & 5, which shows that there is a large concentration near the austenite-allotriomorphic ferrite interface within the time scale of the experiments typical of welding. This chapter describes the results of a series of experiments carried out to change the ratio of allotriomorphic ferrite to austenite grain size, to check the hypothesis of Dallam and Olson. The allotriomorphic ferrite thickness was changed while keeping the austenite grain size constant. The aim was to observe the effect on the acicular ferrite that forms subsequently.

The second feature of the experiments involved the study of the transformation to acicular ferrite during continuous cooling experiments to simulate the behaviour during welding. In practice the welding conditions have to be selected so that a small amount of allotriomorphic ferrite grows before the $B_s$ temperature is reached.
Table 6.1 Details of step heat treatments:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Alloy</th>
<th>$T_1$, °C/ time at $T_1$, s</th>
<th>$T_2$, °C/ time at $T_2$, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>A78ST1</td>
<td>78</td>
<td>700 / 15</td>
<td>530 / 30</td>
</tr>
<tr>
<td>A78ST2</td>
<td>78</td>
<td>700 / 30</td>
<td>530 / 30</td>
</tr>
<tr>
<td>A78ST3</td>
<td>78</td>
<td>700 / 45</td>
<td>530 / 30</td>
</tr>
<tr>
<td>A77ST1</td>
<td>77</td>
<td>700 / 90</td>
<td>500 / 30</td>
</tr>
<tr>
<td>A77ST2</td>
<td>77</td>
<td>700 / 120</td>
<td>500 / 30</td>
</tr>
<tr>
<td>A77ST3</td>
<td>77</td>
<td>700 / 240</td>
<td>500 / 30</td>
</tr>
</tbody>
</table>

6.2 Experimentation

As mentioned above, the aim was to examine the effect of carbon partitioning during allotriomorphic ferrite formation on the subsequent transformation to acicular ferrite. Alloys 77 and 78 (Table 2.2), which differ in chromium concentrations, were used, the preparation techniques being described in chapter 2.

Table 6.1 describes the step heat treatments, where the residual austenite carbon concentrations were expected to change with different transformation times at $T_1$. The heat treatments were carried out using the Theta-Industries high speed dilatometer. In all cases the austenitisation temperature was 1150 °C and time was 10 minutes. The austenite grain size for this treatment was measured to be around 78 μm ± 10. The transformation temperature $T_2$ (below $B_s$ where acicular ferrite can nucleate on inclusions) and time at $T_2$ were kept the same for a particular alloy composition. The time at $T_2$ was chosen to be small to avoid extensive growth. The cooling between $T_1$ and $T_2$ was achieved using a helium gas jet. Partial transformation at $T_2$ followed by quenching to ambient temperature facilitated the identification of ferrite plates. The nucleation density of acicular ferrite was estimated by counting the plates in a square grid of 20 x 20 μm. Table 6.2 summarises the continuous cooling transformation studies. The hardness was measured using a Leitz microhardness tester with a force of 0.981 N.

6.2.1 Interpretation of Dilatometric Data:

The relative length change $\Delta L/L$ vs temperature ($T$) curve was differentiated numerically with respect to temperature. The slope was calculated by regressing over 10 points on each side of the temperature of interest. The interval between each point being 1 °C. The differentiated curve is expected to show a constant value $e_\alpha$ in the absence of transformation and another constant value $e_\gamma$ when transformation is completed. The transformation start and finish temperatures

113
Table 6.2 Continuous cooling transformation experiments:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Alloy</th>
<th>Cooling Rate °Cs⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>A78CCT1</td>
<td>78</td>
<td>5</td>
</tr>
<tr>
<td>A78CCT2</td>
<td>78</td>
<td>20</td>
</tr>
<tr>
<td>A78CCT3</td>
<td>78</td>
<td>50</td>
</tr>
<tr>
<td>A77CCT1</td>
<td>77</td>
<td>1</td>
</tr>
<tr>
<td>A77CCT2</td>
<td>77</td>
<td>5</td>
</tr>
</tbody>
</table>

can be measured from the deviations from constancy. Previous researchers on CCT behaviour of steel have used $\Delta T$ versus $T$ curve directly to measure these points (Lee and Hon 1987, Ferrante and Farrar, 1982 and Farrar and Harrison, 1987). Eldis (1977) pointed out the uncertainty of measuring the transformation finish temperatures of bainite. The bainite and acicular ferrite can transform from carbon enriched austenite below the $M_s$, of the average alloy composition. Hence, a temperature at which the maximum rate of transformation takes place, $T^*$ is measured as a parameter characterising the acicular ferrite or bainite reaction.

6.3 Results

Samples with differing ratios of allotriomorphic ferrite thickness to austenite grain size ($q / R_a$) revealed no systematic change in the number density of acicular ferrite plates (Fig. 6.1). The measured densities of acicular ferrite plates are presented in Table 6.3. The table also contains the volume fraction of allotriomorphic ferrite. The diffusion distance when allotriomorphic ferrite growth stopped (the distance for the carbon composition to drop from $x^{\omega}_{\omega}$ to $x_c$ in front of the $\alpha/\gamma$ interface) was calculated using equation 4.3. Calculations were carried out for A78ST3 and A77ST3. The effective diffusion distance was found to be 14 and 17 μm so that a substantial region in front of the interface should be transformation free. Figure 6.2 shows the transformation free zone near to the $\alpha/\gamma$ interface. The zone dimensions are comparatively smaller than the diffusion distance values calculated, because the transformation to bainite is stifled near to the transformation interface, the dimensions of which are much smaller than the diffusion distance.

Figure 6.3 shows the measured $\Delta T$ vs $T$ curves and the corresponding numerically differentiated curves of the continuous cooling transformation experiments. The transformation start and finish temperatures were measured from these graphs (Table 6.4). The corresponding micrographs are presented in Fig. 6.4. The relative length change plots of A77CCT1 and
Table 6.3 Measured thickness of allotriomorphic ferrite and acicular ferrite plate density.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>allotriomorphic ferrite</th>
<th>acicular ferrite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>half thickness</td>
<td>volume</td>
</tr>
<tr>
<td></td>
<td>μm</td>
<td>%</td>
</tr>
<tr>
<td>A78ST1</td>
<td>3-5</td>
<td>12</td>
</tr>
<tr>
<td>A78ST2</td>
<td>6-9</td>
<td>22</td>
</tr>
<tr>
<td>A78ST3</td>
<td>10-12</td>
<td>35</td>
</tr>
<tr>
<td>A77ST1</td>
<td>1-3</td>
<td>10</td>
</tr>
<tr>
<td>A77ST2</td>
<td>5-8</td>
<td>19</td>
</tr>
<tr>
<td>A77ST3</td>
<td>12-15</td>
<td>37</td>
</tr>
</tbody>
</table>

A77CCT2 are presented in Fig. 6.5 and corresponding microstructures in Fig. 6.6. The micrographs clearly show that for the higher cooling rates the austenite grain boundaries are only partially decorated with allotriomorphic ferrite, causing a bainitic microstructure. A detailed study of the microstructures of A78CCT2 and A78CCT1 indicated an apparent change in plate size. The plate size of A78CCT1 (5.3 ± 0.8) was higher than the plate size of A78CCT2 (4.1 ± 0.6), measured using the random mean linear intercept technique on optical micrographs, and corresponding hardness values were found to be 273 HV and 286 HV respectively.

Table 6.4 Characterisation of continuous cooling experiments. The parameters are discussed in the text.

<table>
<thead>
<tr>
<th>Exp No</th>
<th>Δts00−500 seconds</th>
<th>Allotriomorphic ferrite Tₕ−Tₑ °C</th>
<th>Tᵢᵃᶜᵢᶜ/ᵦᵃⁱⁿ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A78CCT1</td>
<td>76</td>
<td>740-640</td>
<td>600</td>
</tr>
<tr>
<td>A78CCT2</td>
<td>25</td>
<td>710-615</td>
<td>565</td>
</tr>
<tr>
<td>A78CCT3</td>
<td>21.5</td>
<td>710-640</td>
<td>585</td>
</tr>
<tr>
<td>A77CCT1</td>
<td>300</td>
<td>760-620</td>
<td>545</td>
</tr>
<tr>
<td>A77CCT2</td>
<td>60</td>
<td>750-650</td>
<td>520</td>
</tr>
</tbody>
</table>

†Tₛₑ stand for start and end transformation temperatures.
6.4 Discussion

The results show that the enrichment of austenite takes place only locally, near the α/γ interface as supported by the transformation free zones observed near to the interface (Fig. 6.2). Thus, the reported variation of plate size by Dallam and Olson (1989) and the results of Fleck et al., (1986) still remains to be explained.

On the other hand, the microstructure of the continuously cooled specimens showed an apparent change in the acicular ferrite plate size. A78CCT1 (slow cooling rate) showed coarse plates when compared with A78CCT2 (high cooling rate). The scale of the size variation is comparable to variations published by Dallam and Olson (1989) and Fleck et al., (1986). Coarser acicular ferrite was associated with higher $T_{acfc}^i=600$ °C compared to finer acicular ferrite size $T_{acfc}^i=560$ °C. The allotriomorphic ferrite was found to be around 25% in the case of A78CCT1 compared with 14% in the case of A78CCT2. The volume fractions are smaller, so the plate size variation cannot be attributed to the enrichment of austenite. The results indicate, however, that there is a strong relation between the transformation temperature and the acicular ferrite plate size. This result is similar to the reported variation of plate size with transformation temperature for bainitic laths (Ohmori et al., 1971). Thus the development of acicular ferrite plates show another similarity with bainite.

Irrespective of the mechanism of the reduction of plate size, the results showed that the finer acicular ferrite is associated with a lower transformation temperature. Thus, welds should be designed in such a way that the maximum extent of transformation occurs at lower transformation temperatures. This can be achieved in welds only by increasing the cooling rate or altering the alloy chemistry. Too large a cooling rate causes a transition from acicular ferrite to bainite (A78CCT3, Fig. 6.5 & A77CCT2, Fig. 6.6). The results are consistent with diagrams published by Harrison and Farrar (1987b), who found that an increased cooling rate leads to an abrupt increase in volume fraction of bainitic ferrite (referred as lath ferrite), with a drop in allotriomorphic ferrite (Fig. 6.7).

6.5 Conclusions

Changes in the acicular ferrite plate size during continuous cooling are probably due to corresponding changes in transformation temperatures rather than due to any enrichment of the austenite by prior transformation to allotriomorphic ferrite.
Fig. 6.1 The microstructure obtained after step heat treatments (Table 6.1). The microstructures show no apparent change in number of acicular ferrite plates per unit area. (a) A78ST1, (b) A78ST2, (c) A78ST3.
Fig. 6.1 continued
(d) A77ST1, (e) A77ST2, (f) A77ST3.
Fig. 6.2 The microstructure of (a) A78ST3 and (b) A77ST3 indicating a transformation free zone near to $\alpha/\gamma$ interface. Dark regions are the martensite transformed from the enriched austenite near to the interface.
Fig. 6.3 The plots of relative length change, $\frac{dL}{L}$, with temperature, $T$. The solid lines are numerically differentiated curves and the dotted lines are the original curve. The allotriomorphic ferrite transformation start and end temperatures are marked. The inflection temperature point for acicular ferrite reaction is also marked. The plots clearly show the transformation sequences of allotriomorphic ferrite and acicular ferrite. (a) A78CCT1, (b) A78CCT2, (c) A78CCT3.
Fig. 6.4 The microstructure corresponding to the continuous cooling transformation experiments in alloy 78 (see Table 6.2). Note the development of bainite in the case of A78CCT3 and also the apparent change in plate size with A78CCT2 and A78CCT1. (a) A78CCT1, (b) A78CCT2, (c) A78CCT3.
Fig. 6.5 The plots of relative length change, $\Delta L/L$ with temperature, $T$. The solid lines are numerically differentiated curve and the dotted lines are original curve (a) A77CCT1, (b) A77CCT2.
Fig. 6.6 The microstructure corresponding to the continuous cooling transformation experiments in alloy 77 (see Table 6.2). (a) A77CCT1, (b) A77CCT2.
Fig. 6.7 Published CCT and microstructural development diagram of Harrison and Farrar (1987b), indicating the sensitivity of the acicular ferrite reaction to $\Delta t_{800-500}$. 
Chapter 7

A Direct Study of Grain Boundary
Allotriomorphic Ferrite Crystallography

7.1 Introduction

The work presented in the previous chapters has emphasised a beneficial role of thin layers of allotriomorphic ferrite layers on removing the austenite grain surfaces as potential nucleation sites for bainite, and hence for a microstructural transition from bainite to acicular ferrite when suitable intragranular nucleation sites are available in sufficient numbers (Fig. 4.13c). This beneficial effect of allotriomorphic ferrite has to be balanced against its undesirable ability to stimulate the formation of Widmanstätten ferrite or bainite.

When Widmanstätten ferrite grows from allotriomorphic ferrite, it is contiguous with the latter. Thus, allotriomorphic ferrite can only develop into Widmanstätten ferrite if it has the “right” orientation relationship with the austenite, since Widmanstätten ferrite is a product of displacive transformation. This orientation lies within the so-called “Bain region”, within which no plane or direction is rotated by more than about 11° from the Bain orientation (Crosky et al., 1980). The classical Kurdjumov–Sachs (KS) and Nishiyama–Wasserman (NW) orientation relationships lie within this region. The crystallography of allotriomorphic ferrite is therefore of crucial importance in determining whether its presence will have the desired effect of facilitating intragranular nucleation of acicular ferrite, or the undesirable effect of providing a substrate for the nucleation of Widmanstätten ferrite. It is almost certain that grain boundary allotriomorphic ferrite, when it nucleates, has a good fitting orientation relationship (within the Bain region) with one of the austenite grains with which it is in contact. The ferrite grows, however, by reconstructive transformation. The rate of growth would be faster at incoherent interfaces, i.e., in those austenite grains with which the ferrite is “randomly” orientated. The growth process could thus lead to a situation in which the majority of allotriomorphic ferrite/austenite interface is incoherent and hence incapable of developing into Widmanstätten ferrite.

The purpose of the present work was to determine the fraction of ferrite allotriomorphs which, as a consequence of the wrong crystallography generated by selective growth, are unlikely to lead to Widmanstätten ferrite formation. Similar crystallographic experiments have been reported previously (King and Bell, 1975), but the austenite orientation was deduced indirectly by assuming specific habit plane indices for Widmanstätten ferrite plates, indices which are now known to be different (Watson and McDougall, 1973). Experiments have been designed here which allow the retention of large quantities of austenite permitting the direct measurement of its orientation.
7.2 Experimental Methods

7.2.1 Alloys and Heat Treatment

The chemical compositions (wt.%) of the two Fe–C–Si–Mn alloys studied are given in Table 7.1. The steels were prepared as 20 kg vacuum induction melts from high purity base materials. The ingots were forged and hot rolled to 10 mm diameter rods, followed by swaging to 3 mm diameter rods. They were then homogenised at 1200 °C for 3 days while sealed in quartz capsules containing pure argon.

In low alloy steel, usually on cooling to room temperature, there will be very small amounts of retained austenite. The aim of the present work has been to study the crystallography of allotriomorphic ferrite directly with austenite. Hence, the steel studied is of wrought alloy and different composition from the alloy used in previous chapter. The relatively high silicon concentration of the alloys ensures that carbides do not precipitate during the formation of upper bainite (Bhadeshia and Edmonds, 1979). Consequently, the carbon that is partitioned into the residual austenite stabilises it to further transformation, with substantial quantities of austenite being retained to ambient temperature. This austenite is of value in directly assessing the crystallography of any transformation products. Two-stage step heat treatments were designed to take advantage of this characteristic, to obtain mixed microstructures of allotriomorphic ferrite, bainitic ferrite and retained austenite. After austenitisation, the samples were partially isothermally transformed to a small volume fraction of allotriomorphic ferrite at a temperature $T_1$, followed by a second isothermal heat treatment at a lower temperature $T_2$ in order to induce the formation of upper bainitic ferrite. The amount of allotriomorphic ferrite was kept small in order to study the early stages of the reaction, before impingement between different allotriomorphs can confuse interpretation. Consequently, it is the subsequent growth of bainitic ferrite which leads to a larger extent of carbon enrichment in the residual austenite, necessary to prevent much of the untransformed austenite at $T_2$ from decomposing martensitically during the final quench to ambient temperature. The treatment at $T_1$ was in some cases omitted in order to study the crystallography of bainite in its own right.

7.2.2 Metallography

Thin foil samples for transmission electron microscopy were prepared using the procedure outlined in chapter 2. The samples were examined in Philips EM300 and EM400T transmission electron microscopes operated at 100 and 120 kV respectively.

Figure 7.1a shows the optical micrograph of allotriomorphic ferrite along the austenite grain boundaries and Fig. 7.1b shows typical bainitic sheaves observed within the austenite grain grains. Microanalysis experiments were carried out on the EM400T, using an energy
Table 7.1 Chemical composition (wt.%) and details of the heat treatments. The austenitisation conditions were 1000 °C/5 min.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>(T_1 \text{ °C/Time} )</th>
<th>(T_2 \text{ °C/Time} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.40</td>
<td>2.03</td>
<td>3.00</td>
<td>703/10 h</td>
<td>340/12 h</td>
</tr>
<tr>
<td>A2</td>
<td>0.22</td>
<td>2.03</td>
<td>3.00</td>
<td>640/1 h</td>
<td>340/140 min</td>
</tr>
</tbody>
</table>

dispersive X-ray analysis facility. The specimens, which were about 100 nm thick, were held in a beryllium holder tilted 35° from the normal. The X-ray count rate was optimised at about 1000 counts s\(^{-1}\), over a count period of 100 s. The data were analysed using the LINK RTS 2 FLS program for thin foil microanalysis; this corrects the data for atomic number and absorption effects and accounts for overlapping peaks by fitting standard profiles. Even though the probe diameter was about 2.5 nm, beam spreading due to the scattering of electrons within the thin foil gave an estimated broadened beam diameter of about 20 nm, a size which was small enough for the purposes of the investigation.

7.3 Crystallographic Technique

Austenite/ferrite orientations outside the Bain region generally arise during reconstructive transformation in which growth is not restricted by austenite grain boundaries, so that a particle can grow into regions which had little or no influence in determining its orientation during the nucleation stage. Although the ferrite may nucleate from austenite with an orientation within the Bain region, it can then grow with a random orientation into adjacent austenite grains. The probability of finding ferrite which is well related to the adjacent austenite depends therefore on the growth stage; the aim here is to detect whether or not the orientation of ferrite which has grown well beyond the nucleation stage has an orientation within the Bain region, since only then is it capable of nucleating secondary Widmanstätten ferrite plates. To distinguish the Bain region from random orientations does not require extreme precision of the kind associated with Kikuchi line measurements. The experimental data presented here are based on an analysis of the reciprocal lattice vectors observed in conventional selected area electron diffraction patterns. The zone axis of each pattern can then deviate typically by 5° from the optic axis of the microscope, and this can be used as an estimate of the error. In fact, the error should be somewhat smaller since the orientations were deduced not from the zone axes, but by examining the relationship between pairs of reciprocal lattice vectors (in the same diffraction pattern) from each of the two crystals concerned. The four reciprocal lattice vectors
were then used to determine the coordinate transformation matrix defining the orientation relationship, in the manner described elsewhere (Yang and Bhadeshia, 1989a and Bhadeshia, 1987b).

The validity of the method was checked by measuring the orientation relationship between bainitic ferrite and its parent austenite; the displacive transformation mechanism ensures that the orientation should always lie well within the Bain region, with a pair of corresponding close-packed planes and a pair of corresponding close-packed directions within those planes being approximately parallel. Data from 16 sets of measurements are summarised in Fig. 7.2, where the angle between the close-packed planes \(\{111\}_\gamma\) and \(\{011\}_\alpha\) is designated \(\theta\), and that between the directions \(<10\overline{1}>_\gamma\) and \(<11\overline{1}>_\alpha\) is designated \(\phi\). The data are, as expected, all within the Bain region. The mean value of the angle \(\theta\) was found to be 2.5° with a standard deviation of 1.9° whereas the corresponding mean and standard deviation for \(\phi\) were 3.4 and 2.0° respectively. Given that \(\theta\) is expected to be very close to zero (within about 0.5°), the analysis confirms that the error associated with the technique is small enough to distinguish between random and Bain-region orientations.

7.4 Results and Discussion

7.4.1 Allotriomorphic Ferrite/Austenite Orientation Relations

Figure 7.3 revealed that the two-stage heat treatment resulted in the desired microstructure, consisting of small allotriomorphs of ferrite at the austenite grain boundaries, and sheaves of bainitic ferrite and retained austenite. Facets which appeared to be growth ledges were observed on the allotriomorphic ferrite indicated by the arrow in Fig. 7.3, on the side of the allotriomorph which had a near KS relation with the austenite. An other remarkable example of the crystallographic data obtained using transmission electron microscopy and electron diffraction is presented in Fig. 7.4 which will be discussed in detail after a presentation of all the crystallographic data. Occasionally, the allotriomorphic ferrite in alloy A1 seemed to contain manganese rich, unidentified carbides as seen in Fig. 7.5 and Table 7.2.

The complete set of crystallographic data are presented in Tables 7.3 & 7.4, for alloys A1 and A2 respectively. In these tables, an “a” appearing after the identification number represents the orientation relationship between the allotriomorph and the adjacent austenite grain \(\gamma_1\), whereas “b” denotes the orientation of the same allotriomorph with respect to the other austenite grain \(\gamma_2\) with which it is in contact. We also adopt the convention here that the \(\alpha/\gamma_1\) orientation is chosen to be the one that is better with respect to lattice matching than the \(\alpha/\gamma_2\) orientation. In one particular case, where the ferrite was found at a three-grain junction, a letter ‘c’ was used to identify its orientation with the third austenite grain. The orientation
Table 7.2. Microanalysis data on allotriomorphic ferrite, bainite and carbide on alloy A1 & A2 after step heat treatment. The compositions of the austenite and ferrite in equilibrium were calculated using the National Physical Laboratory MTDATA system (1989). Note the absence of partitioning for bainitic ferrite, confirming the microanalysis technique.

<table>
<thead>
<tr>
<th>Allotriomorphic ferrite</th>
<th>Element</th>
<th>Observed</th>
<th>Equilibrium</th>
<th>Alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
<td>1.6</td>
<td>1.00</td>
<td>A1 (703 °C)</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>2.5</td>
<td>2.68</td>
<td>A1 (703 °C)</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>1.8</td>
<td>1.16</td>
<td>A2 (640 °C)</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>1.9</td>
<td>2.40</td>
<td>A2 (640 °C)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bainitic ferrite</th>
<th>Element</th>
<th>Observed</th>
<th>Expected</th>
<th>Alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
<td>3.1</td>
<td>3.00</td>
<td>A1</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>2.0</td>
<td>2.03</td>
<td>A1</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>3.2</td>
<td>3.00</td>
<td>A2</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>2.3</td>
<td>2.03</td>
<td>A2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Element</th>
<th>Observed</th>
<th>Expected</th>
<th>Alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
<td>12.6</td>
<td>-</td>
<td>A1</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>0.4</td>
<td>-</td>
<td>A1</td>
</tr>
</tbody>
</table>

data are summarised for convenience in terms of the angles $\theta$ and $\phi$ defined earlier, although the full coordinate transformation matrix which completely defines the $\alpha/\gamma$ orientation relation was available for each case. They results are also illustrated graphically in Fig. 7.6.

Out of a total of 19 cases examined in detail each case consisting of an allotriomorphic ferrite and its adjacent $\gamma$ grains, only 7 were consistent with an $\alpha/\gamma_1$ orientation relation within the Bain region, the majority of the orientation relationships being more or less random. The seven cases were found to be consistent with the C. S. Smith (1948) hypothesis in that the ferrite in each case revealed a tendency to crystallographically facet on the side with the Bain region related austenite, whereas curved boundaries were apparent on the other side with which it was randomly orientated. In only one case was the ferrite orientation such as to be within the Bain region with respect to both of the adjacent austenite grains within the limits of experimental error (Case 15, Table 7.3).
Only a small fraction of allotriomorphs are therefore found to be in the right crystallographic orientation to provide a substrate for secondary Widmanstätten ferrite growth (the fact that Widmanstätten ferrite did not form is because the alloys were heat-treated above the Widmanstätten ferrite start temperature). It is very likely that this result cannot be attributed to the orientation relationships that develop during nucleation. In order to avoid a large activation barrier, the ferrite must nucleate with a good match with at least one of the austenite grains with which it is in contact (Aaronson and Russel, 1981). Nucleation would therefore demand that all allotriomorphs should exhibit orientations within the Bain region. However, the original orientation distribution will be changed if the allotriomorphs grow into regions far from their original nucleation sites. This can happen if growth occurs at a higher rate along those austenite grains boundaries with which the ferrite has high energy (i.e., high mobility) interfaces. Purdy (1978), using hot-stage transmission electron microscopy, has directly demonstrated the higher mobility of interfaces between ferrite and austenite which are randomly orientated. The smaller extent of ferrite penetration into the Bain region related austenite (Fig. 7.4), compared with growth into the other randomly orientated austenite grain is consistent with Purdy's work.

The orientation data (Tables 7.3 & 7.4) are consistent with the earlier studies of Ryder and Pitsch (1966) and King and Bell (1975). Although the present work reveals a rather smaller fraction of allotriomorphs with an orientation within the Bain region, any quantitative comparisons are doubtful since the crystallographic textures of the materials used are unlikely to be identical. The texture must influence the relative orientations of the austenite grains and hence the crystallography of the ferrite that forms subsequently. This may also explain why King and Bell found a larger fraction of allotriomorphs with a good match with both the adjacent austenite grains.

7.4.2 Ferrite Orientation with Respect to Both Adjacent Austenite Grains

It is only by coincidence that a ferrite grain nucleates with a reproducible orientation relationship with both of the austenite grains with which it is in contact. In general, it is only expected to have an orientation relationship with one of the parent austenite grains. It nevertheless seems reasonable that the ferrite should attempt to choose a variant of this orientation relation which allows the highest degree of matching with the other austenite grain, even though its orientation with the second grain may not be ideal.

The seven cases for which the ferrite was found to have an orientation within the Bain region (Tables 7.3 & 7.4) were analysed further to study whether the ferrite makes any attempt during nucleation to optimise lattice matching with both the austenite grains. For the other data, the crystallography suggests that the allotriomorphs have grown away from their original
Table 7.3. Summary of $\alpha - \gamma$ orientation relationship in alloy A1.

<table>
<thead>
<tr>
<th>Number</th>
<th>$\theta$</th>
<th>$\phi$</th>
<th>Approx. Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>4.04</td>
<td>3.2</td>
<td>KS/NW</td>
</tr>
<tr>
<td>1b</td>
<td>27.6</td>
<td>22.0</td>
<td>-</td>
</tr>
<tr>
<td>2a</td>
<td>0.0</td>
<td>5.0</td>
<td>NW</td>
</tr>
<tr>
<td>2b</td>
<td>18.1</td>
<td>32.1</td>
<td>-</td>
</tr>
<tr>
<td>3a</td>
<td>15.1</td>
<td>4.9</td>
<td>-</td>
</tr>
<tr>
<td>3b</td>
<td>13.7</td>
<td>13.6</td>
<td>-</td>
</tr>
<tr>
<td>4a</td>
<td>0.0</td>
<td>5.3</td>
<td>NW</td>
</tr>
<tr>
<td>4b</td>
<td>19.9</td>
<td>15.8</td>
<td>-</td>
</tr>
<tr>
<td>4c</td>
<td>35.3</td>
<td>33.5</td>
<td>-</td>
</tr>
<tr>
<td>5a</td>
<td>2.0</td>
<td>5.5</td>
<td>KS/NW</td>
</tr>
<tr>
<td>5b</td>
<td>20.5</td>
<td>16.4</td>
<td>-</td>
</tr>
<tr>
<td>6a</td>
<td>15.0</td>
<td>16.8</td>
<td>-</td>
</tr>
<tr>
<td>6b</td>
<td>18.9</td>
<td>22.5</td>
<td>-</td>
</tr>
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<td>7a</td>
<td>8.7</td>
<td>10.7</td>
<td>-</td>
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<tr>
<td>7b</td>
<td>24.5</td>
<td>10.1</td>
<td>-</td>
</tr>
<tr>
<td>8a</td>
<td>5.7</td>
<td>23.5</td>
<td>-</td>
</tr>
<tr>
<td>8b</td>
<td>28.9</td>
<td>28.5</td>
<td>-</td>
</tr>
<tr>
<td>9a</td>
<td>0.0</td>
<td>19.8</td>
<td>-</td>
</tr>
<tr>
<td>9b</td>
<td>24.3</td>
<td>10.6</td>
<td>-</td>
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<td>10a</td>
<td>18.7</td>
<td>11.3</td>
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<td>10b</td>
<td>26.4</td>
<td>26.4</td>
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<td>11a</td>
<td>14.4</td>
<td>17.0</td>
<td>-</td>
</tr>
<tr>
<td>11b</td>
<td>25.5</td>
<td>23.8</td>
<td>-</td>
</tr>
<tr>
<td>12a</td>
<td>28.5</td>
<td>21.4</td>
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<td>12b</td>
<td>21.4</td>
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<td>13a</td>
<td>30.3</td>
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<td>13b</td>
<td>24.4</td>
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<tr>
<td>14a</td>
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<tr>
<td>14b</td>
<td>2.7</td>
<td>28.7</td>
<td>-</td>
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<tr>
<td>15a</td>
<td>3.0</td>
<td>5.8</td>
<td>KS/NW</td>
</tr>
<tr>
<td>15b</td>
<td>6.9</td>
<td>5.3</td>
<td>$\approx$ KS/NW</td>
</tr>
</tbody>
</table>
Table 7.4 Summary of $\alpha - \gamma$ orientation relationships for alloy A2.

<table>
<thead>
<tr>
<th>Number</th>
<th>$\theta$</th>
<th>$\phi$</th>
<th>Approx. Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>0.9</td>
<td>21.0</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>20.1</td>
<td>20.1</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>14.2</td>
<td>13.0</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>25.7</td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>3.9</td>
<td>6.2</td>
<td>KS/NW</td>
</tr>
<tr>
<td>3b</td>
<td>27.3</td>
<td>26.2</td>
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</tr>
<tr>
<td>4a</td>
<td>3.8</td>
<td>5.6</td>
<td>KS/NW</td>
</tr>
<tr>
<td>4b</td>
<td>23.6</td>
<td>31.5</td>
<td></td>
</tr>
</tbody>
</table>

sites, the observed orientations no longer being representative of the nucleation stage.

The degree of $\alpha/\gamma_2$ fit was assessed by calculating the determinant of the matrix $T$, which represents the ratio of the volume of the unit cell of the Bollmann's O-lattice to that of volume of the unit cell of the reference crystal. The O-lattice is a set of points of perfect fit between the two crystal lattices which are allowed notionally to interpenetrate and fill all space. Hence, the smaller the value of the determinant, the better is the fit between the two crystals. The matrix $T$ can be deduced from a knowledge of the deformation $S$ which converts the lattice of one of the crystals into that of the other (the reference lattice). The deformation $S$ can be deduced from a knowledge of the coordinate transformation matrix $J$ (representing the orientation relationship) and an assumed correspondence matrix $C$. $J$ is of course, measured experimentally whereas $C$ is taken to be the Bain correspondence; the magnitude of the deformation $S$ depends on the specific variant of the Bain correspondence, which in each case is chosen to be that which leads to the smallest determinant of $T$. Details of these methods can be found in reference (Christian, 1975).

Considering a $\gamma_1/\alpha/\gamma_2$ tricrystal, in which the $\gamma_1/\alpha$ orientation is within the Bain region, the symmetry of cubic crystals suggests that there are in general, twenty four variants of $(\alpha J \gamma_1)$; of these twenty four possibilities, one corresponds to the experimentally measured orientation, and the task here is to discover whether this particular variant of the orientation relationship also gives the best match with the crystal $\gamma_2$, i.e., the one which gives the smallest value of the determinant of $(\gamma_2 T \gamma_2)$, where

$\dagger$ The notation used here is due to Bowles and Mackenzie (1954), and suggests that $J$ is a $3 \times 3$ coordinate transformation matrix describing the orientation relationship between $\alpha$ and $\gamma_1$. Each column of $J$ represents the components of a basis vector of $\gamma_1$ in the basis $\alpha$. 

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\[(\gamma_2 \ T \ \gamma_2) = I - (\gamma_2 \ C \ \alpha)(\alpha \ J \ \gamma_2).\] (7.1)

In none of the seven cases examined did the allotriomorph seem to attempt to lattice match with both of the adjacent austenite grains. Thus, the experimental variant of the \((\alpha \ J \ \gamma_1)\) orientation did not correspond to the smallest possible value of the determinant of \((\gamma_2 \ T \ \gamma_2)\), as illustrated in Fig. 7.7. The ratio of calculated minimum determinant value for \((\gamma_2 \ T \ \gamma_2)\) for a given variant and the actual determinant value observed for \((\gamma_2 \ T \ \gamma_2)\) is presented in Fig. 7.8, which summarises the variant analysis. The result is difficult to explain, but could indicate that the orientation of the austenite grain boundary plane might have an effect on the choice of the orientation variant (Aaronson and Russel, 1981).

7.4.9 Bainite/Austenite Grain Boundary Crystallography

The opportunity was taken during the allotriomorphic ferrite experiments, to measure also the orientations of grain boundary nucleated bainite and the adjacent austenite grains (Table 7.5). Similar to the results obtained for allotriomorphic ferrite, the bainite did not seem to choose an orientation variant with its parent austenite which gave the optimum matching with the other austenite grain.

| Table 7.5: Alloy A1. Summary of bainite orientation relationship with the austenite grain in which it is growing (a), and with the grain on the other side of the boundary (b). |
|---|---|---|---|
| Number | \(\theta\) | \(\phi\) | Approx. Orientation |
| 1a | 0.0 | 5.3 | NW |
| 1b | 10.5 | 10.3 | - |
| 2a | 0.0 | 0.5 | KS |
| 2b | 11.4 | 0.0 | - |
| 3a | 0.7 | 0.0 | KS |
| 3b | 3.3 | 0.0 | KS/NW |
| 4a | 4.3 | 6.4 | KS/NW |
| 4b | 0.7 | 5.3 | NW |
| 5a | 0.06 | 0.0 | KS |
| 5b | 14.9 | 0.0 | - |
| 6a | 0.0 | 0.06 | KS |
| 6b | 15.0 | 0.0 | - |

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7.4.4 Detailed Examination of a Particular Allotriomorph

One of the experiments (Case 1, Table 7.3) revealed an exceptionally good example of an allotriomorph which exhibited microstructural features consistent with its $\alpha/\gamma_1$ orientation being well within the Bain region, and a random $\alpha/\gamma_2$ orientation (Fig. 7.4). With the $\gamma_1$ grain, the ferrite exhibited a very pronounced tendency to crystallographically facet, giving a clearly ledged transformation interface. Whether these ledges are growth ledges, or simply facetting which results from tendency of the particle to minimise interfacial energy, can only be decided by observing the growth. Their non-uniform height and spacing (Fig. 7.9) is consistent with theory for ledged growth (Atkinson, 1982), but such variations can also be expected from facetting. The important point is that the facets represent planes of low interfacial energy around the particle.

The crystallographic indices of the facet planes were measured using a method of trace analysis which avoids ambiguity. Because the interface planes were inclined to the foil surface, their projected widths within the foil and contrast conditions can be used to measure their inclinations, which can in turn be used to fix the interface plane uniquely; the fringe contrast also helps to fix the sense of inclination of the interface plane. The results are plotted on Fig. 7.10, which also illustrates the interfacial energy minima calculated by Ecob and Ralph (1981). It is evident from Fig. 7.10, that within the limits of experimental error, the present data are approximately consistent with those calculations.

A further interesting feature is that the $\alpha/\gamma_1$ side of the boundary has been able to nucleate a plate of bainite (Fig. 7.4 & 7.11) during the second stage of the heat-treatment (below the bainite-start temperature). This is consistent with the discussion earlier that only allotriomorphs whose orientation lies within the Bain region can be active in nucleating the products of displacive transformation (e.g. bainite, Widmanstätten ferrite). By contrast, a transformation-free region is observed on the other side ($\alpha/\gamma_2$) where the allotriomorph is randomly orientated. It is also interesting to note that the trace of the bainite habit plane for the plate nucleated from the allotriomorph does not coincide with the facet planes on the allotriomorph (Fig. 7.11). The bainite habit plane should be determined by the minimisation of strain energy due to the shape change accompanying transformation, rather than interfacial energy minimisation.

7.4.5 Chemical Composition of Allotriomorphic Ferrite

It is of interest to examine the chemical composition of the allotriomorphic ferrite formed in the two alloys because the alloys A1 and A2 had respectively been heat-treated at temperatures above and below the paraequilibrium $\text{Ae}_3'$ curve of the phase diagram (Fig. 7.12). Paraequilibrium is a condition of constrained equilibrium in which the iron to substitutional solute atom ratio is constant everywhere during transformation, but subject to that constraint,
the carbon attains the same chemical potential in all phases. Thus, the Ae$3'$ curve defines the composition of the austenite which is in paraequilibrium with ferrite. The curves presented in Fig. 7.12, and the thermodynamic calculations presented in Table 7.2, were calculated as in references (MTDATA, 1989 and Bhadeshia and Edmonds, 1980). The experimental data presented in Table 7.2 represent the bulk chemical compositions of the ferrite allotriomorphs, and conclusively demonstrate that both the manganese and silicon partition during the growth of ferrite in both the alloys, for the transformation conditions described earlier. Furthermore, although partitioning is found, its extent is less than that expected from equilibrium considerations (Table 7.2) and the growth process is best described as nonequilibrium.

For the transformation conditions used, it is thermodynamically impossible for the ferrite in alloy A1 to grow by a paraequilibrium mechanism, so that the partitioning of manganese and silicon is necessary during transformation. Since alloy A2 was transformed below the Ae$3'$ phase boundary (Fig. 7.12), it is thermodynamically possible for the ferrite to form with paraequilibrium; this does not however, rule out growth with local equilibrium at the interface, or indeed with any of an infinite set of conditions between equilibrium and paraequilibrium. The exact mode of transformation must be decided by kinetic considerations. A method for estimating the transition from equilibrium to paraequilibrium involves the calculation of the extent $z$ of the diffusion field of the solute element (Coates, 1973a):

$$z \simeq \frac{2D}{v}$$

(7.2)

where $D$ is the diffusivity of the solute concerned in the parent phase, and $v$ is the interfacial velocity, which for the present circumstances is time dependent ($v = \alpha_1 t^{-0.5}$, where $\alpha_1$ is the one-dimensional parabolic thickening rate constant and $t$ is the growth time). Coates suggested that if $z$ is found to be less than about 1 nm, then growth could be assumed to occur by a paraequilibrium mode, since the diffusion distance is then negligible.

The velocity was estimated by measuring the mean allotriomorph half-thickness ($q$) and dividing by the isothermal transformation time. This might lead to an underestimation of $v$ since an incubation period may be necessary before the nucleation of ferrite, an approximation which would lead to an overestimation of $z$. The values of $z$ were found to be $z_{Mn} \simeq 18$ nm and $z_{Si} \simeq 4$ nm for alloy A1 in which the transformation was carried out at the higher temperature (above Ae$3'$). For alloy A2, on the other hand, both of the calculated diffusion distances were found to be incredibly small at $z_{Mn} \simeq 8 \times 10^{-2}$ nm and $z_{Si} \simeq 0.14$ nm. In contradiction to the experimental evidence for alloy A2, this suggests that allotriomorphic ferrite growth should occur by a paraequilibrium mechanism.

As first pointed out by Coates, the diffusion distance criterion for assessing the onset of
paraequilibrium growth is unlikely to be correct, since conventional diffusion theory breaks down as the concentration gradients become large. Hillert (1981) has also pointed out that the criterion fails to predict the experimental observations on pearlite and massive ferrite.

Aziz (1982) has developed a model for solute trapping during rapid solidification, which is likely to be a better representation of nonequilibrium growth (Olson et al., 1990). If the actual ratio (partition coefficient) of the solute concentration in the product to that in the parent phase at the interface is written $k_p$, and the equilibrium ratio $k_e$, he finds that

$$k_p = \frac{1 + \beta k_e}{1 + \beta} \quad (7.3)$$

where $\beta = D/(v\lambda)$, $\lambda$ being the intersite diffusion distance assumed to be 0.25 nm. As $k_p$ tends towards unity, growth tends towards paraequilibrium. For the present experiments, assuming that the measured ferrite concentration can be used to estimate $k_p$, the theory is found to predict correctly that substitutional solute partitioning should occur during the growth of ferrite in alloy A2. The partition coefficients were calculated to be $k_p^{Mn} \approx 0.7$ and $k_p^{Si} \approx 1.7$.

7.5 Summary & Conclusions

By using a steel containing a large silicon concentration, and a two-stage heat treatment procedure, it has been possible to produce a microstructure consisting of allotriomorphic ferrite, bainitic ferrite and retained austenite. This permitted a direct examination of the crystallography of grain boundary allotriomorphs of ferrite. It is found that the fraction of allotriomorphs which have an orientation (with the parent austenite) which is in the Bain region is rather small. This has implications on the theory for the prediction of microstructure in steel welds, where a thin layer of allotriomorphic ferrite is required to promote the intragranular formation of acicular ferrite, as long as it can be prevented from nucleating Widmanstätten ferrite at the same time. This qualitative conclusion has to be backed by further research before the fraction of active allotriomorphs can be predicted. Such work must consider the role of crystallographic texture in the parent austenite, and of its subsequent rate of transformation to allotriomorphic ferrite.

Most of the allotriomorphs do not seem to attempt to maximise lattice matching with both of the grains with which they are in contact, and it is speculated that this might be due to an influence of austenite grain boundary orientation in determining variant selection.

It has been shown that the transition to paraequilibrium growth as the transformation temperature is reduced, cannot be predicted by estimating the extent of the solute diffusion

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1 It is really the concentrations at the transformation interface which are of relevance, so that the calculated values of $k_p$ cannot be compared directly with our experimental data, although they can certainly be used to indicate whether growth should involve a substantial degree of partitioning.
field in the austenite during allotriomorphic ferrite growth. A possible way forward would be to utilise solute trapping theory, in a manner applied already to coupled diffusional/displacive transformations (Olson et al., 1990), to predict the partitioning coefficient as a function of undercooling below the equilibrium transformation temperature.
Fig. 7.1 Microstructure observed in alloy A1 after the step heat treatment as mentioned in Table 7.1

a. Optical micrograph of alloy A1, indicating the allotriomorphic ferrite all along the austenite grain boundaries.

b. Transmission electron micrograph of A1, illustrating the sheaf structure of bainite.
Fig. 7.2 Graphical presentation of summary of $\alpha - \gamma$ orientation relationship for 16 cases of bainite, where $\theta$ is the angle between $\{111\}_\gamma - \{011\}_\alpha$ and $\phi$ is the angle between $<10\bar{1}>_\gamma - <11\bar{1}>_\alpha$. 
Fig. 7.3 Microstructure obtained in alloy A1 after the step heat treatment. (a) Bright field micrograph illustrating allotriomorphic ferrite, bainite and retained austenite, (b) corresponding dark field micrograph for the residual austenite. The inset is the diffraction pattern from the allotriomorphic ferrite and austenite (solid line is ferrite < 001 > zone axis and dotted line is austenite).
Fig. 7.4 (a) Bright field electron micrograph exhibiting an allotriomorphic ferrite nucleated from austenite grain boundary (marked as B), and bainitic sheaves growing from austenite grain boundary and also within the grain. (b) Diffraction pattern from the allotriomorphic ferrite and $\gamma_1$ a near KS/NW orientation relation, (c) the diffraction pattern of austenite $\gamma_2$ from the random orientation side of allotriomorphic ferrite, consisting of other reflections due to bainitic ferrite also. The $\gamma_2$ reflections are used for finding orientation relation ($\alpha J_2$), by overlapping the two diffraction patterns appropriately (see overleaf).
Fig. 7.5 An allotriomorphic ferrite in alloy A1 with carbides. The morphology suggest that the precipitation might have occurred during transformation to ferrite, explaining the apparent coverage by single allotriomorphic grain.
Fig. 7.6 Graphical presentation of summary of $\alpha - \gamma$ orientation relationship, data from Table 7.3 & 7.4, where $\theta$ is the angle between $\{111\}_\gamma - \{011\}_\alpha$ and $\phi$ is the angle between $<10\bar{1}>_\gamma - <11\bar{1}>_\alpha$. 
Fig. 7.7 Plot of variation of determinant value of $T$ matrix, as discussed in the text. The point (for variant 1) indicates the determinant of $T$ matrix obtained using the experimentally observed orientation relationship, $(\alpha J \gamma_2)$.

Fig. 7.8 Summary of variant analysis on allotriomorphic ferrites which exhibited near KS/NW with one of the austenite grain. The ratio of determinant value of observed $(\gamma_2 T \gamma_2)$ to that of calculated minimum determinant value is plotted for all the cases. Prefix 1 & 2 correspond to the data from alloy A1 and A2, respectively (Tables 7.3 & 7.4); ideally a value of 1 is expected to indicate a good fitting with $\gamma_2$ for a given $(\alpha J \gamma_1)$ variant.
Fig. 7.9 The micrograph of the interface which showed KS/NW relation with the austenite, exhibiting ledge type faceted interface. The ledge height can be seen to vary over the width of the ferrite, apparently increasing towards the nucleation site of bainite.
Fig. 7.10 Stereogram plot of interface plane calculations for the allotriomorphic ferrite interface which exhibited KS/NW (case 1 of Table 7.3), and exhibited ledge type interface. The stereogram is overlap of [0 0 1]_\alpha and [0 1 1]_\gamma zone axes. The low energy equilibrium interface planes calculated by Ecob and Ralph (1981) are also plotted.
Fig. 7.11 Enlarged image of Fig. 7.4, indicating the region where bainitic ferrite appears to grow directly from the allotriomorphic ferrite.
Fig. 7.12 Plot of calculated Ae3 and Ae3' phase boundaries for various average alloy carbon concentration for a Fe-2Si-3Mn (wt.%) alloy system (MTDATA, 1989, Bhadeshia and Edmonds, 1980). The square symbols indicate the composition of alloys A1 and A2 and temperature at which they were heat treated to form allotriomorphic ferrite.
Chapter 8

Stress and the Acicular Ferrite Transformation

8.1 Introduction

In spite of the microstructural differences, there is considerable evidence that acicular ferrite and bainite have similar transformation mechanisms. The microstructures differ only because of their nucleation site. Some of the similarities between bainite and acicular ferrite were summarised in section 1.2.6. In addition, results of previous chapters indicated following;
1. Both reactions stop when the austenite carbon concentration reaches a value where it becomes thermodynamically impossible to achieve diffusionless growth (chapter 4).
2. Acicular ferrite only forms below the bainite-start temperature.
3. The elimination of austenite grain surfaces by covering them with inert allotriomorphic ferrite leads to a transition from a bainitic to an acicular ferritic microstructure (chapter 4 & 5).

Transformation to both acicular ferrite and bainite causes displacements which are characterised as invariant–plane strains with large shear components (Fig. 8.1). Consequently, the growth of a plate of acicular ferrite or bainite is confined to a single austenite grain (i.e., it is hindered by a grain boundary) since the coordinated movement of atoms implied by the shape change cannot, in general, be sustained across a border between grains in different crystallographic orientations. A further implication is that plates of acicular ferrite, like bainite, always have an orientation relationship with the parent phase which is within the Bain region. This is not necessarily the case when the transformation occurs by a reconstructive mechanism.

It is this last characteristic, the invariant–plane strain shape deformation, which forms the basis of the present investigation. Such a transformation is displacive, and can be regarded as a deformation mode which in addition to accomplishing a shape change, also alters the nature of the lattice. During transformation induced by a decrease in temperature, it is the chemical driving force which causes the deformation. However, the application of an appropriate external stress can provide a mechanical driving force which stimulates transformation without the need to undercool. Such effects are well established for bainite, where a tensile stress favours the development of crystallographic variants whose shape deformations comply most with the applied stress.

The purpose of this investigation is to verify the existence of a similar effect for acicular ferrite. As will be seen later, the specific kind of stress response investigated provides good evidence for the displacive mechanism of the transformation. Acicular ferrite is a prominent
phase in steel weld metals (primarily because they contain nucleating inclusions). There is a possibility that the residual stresses associated with welding may influence the development of the acicular ferrite microstructure.

The only previous study on the relationship between stress and acicular ferrite in mixed microstructures, is by Dallam and Olson (1989). The stress was mostly generated by cooling constrained samples, the transformation being followed by monitoring the sample diameter. Dallam and Olson concluded that there is little influence on the volume fraction of acicular ferrite.

As discussed later, a much more sensitive method of following stress-affected displacive transformation is to monitor the transformation strains along more than one direction (Bhadeshia et al., 1991).

8.2 EXPERIMENTAL METHOD

Alloy 77 is chosen for this study. The welding conditions and the final deposit chemistry are listed in Table 2.1 and Table 2.2. The weld metal, in the as deposited conditions transforms to a bainitic microstructure, in spite of the presence of numerous inclusions of the kind necessary to nucleate acicular ferrite. This is because, in the absence of any allotriomorphic ferrite at the austenite grain boundaries, the boundaries are free to nucleate bainite which forms at an overwhelming rate and succeeds in stifling the intragranular formation of acicular ferrite. By reheating the weld metal and then partially transforming the austenite at an intermediate temperature ($T_1$) to form a thin, uniform layer of allotriomorphic ferrite at the austenite grain surfaces grain boundary nucleation of bainite can be stifled. Thereby the remainder of the austenite transforms to intragranularly nucleated bainite as the alloy is held at a temperature ($T_2$) below the bainite-start ($B_s$) temperature (chapter 4).

This two-stage heat treatment (Fig. 8.2) provides a convenient way of generating an acicular ferrite microstructure in a controlled manner. The calculated transformation temperatures in chapter 5 are taken as an aid to the design of the heat treatment (Table 8.1). The calculation methods have been discussed before.

The heat treatment can easily be carried out in the Formaster thermomechanical simulator used in the present studies. The machine is equipped to simultaneously monitor and record the diametral ($\Delta R$) and longitudinal strains ($\Delta L$), in addition to time, temperature and load data. It can be programmed to automatically carry out the specified thermomechanical treatments. The samples were in the form of 8 mm diameter cylinders 12 mm in length, made from the weld metal by rolling, swaging and machining (Fig. 2.4). The specimen preparation has been presented in chapter 2. The simulator experiments were carried out with the specimen chamber filled with argon. The rapid temperature changes needed between $T_1$ and $T_2$, and between $T_2$
Table 8.1 Calculated transformation data for alloy 77.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ae_3$</td>
<td>828</td>
</tr>
<tr>
<td>$W_S$</td>
<td>680</td>
</tr>
<tr>
<td>$B_S$</td>
<td>546</td>
</tr>
<tr>
<td>$M_S$</td>
<td>427</td>
</tr>
</tbody>
</table>

and ambient temperature were achieved using argon gas jets. Since the equipment is fully capable of monitoring the transformation during these rapid changes, it was confirmed that no reaction occurred during the gas quenching process, so that all the transformation could be attributed to isothermal reaction at $T_1$ and $T_2$. The thermomechanically treated samples were examined in both their transverse and longitudinal sections using the usual metallographic techniques. The austenite grain sizes were determined to be $151 \pm 23 \mu m$, defined as the mean lineal intercept of random test lines superimposed on the microstructure.

8.2.1 The Applied Stress

The stress was only applied the instant the sample reached $T_2$, in order to influence the development of acicular ferrite. It was intended in this work to limit the applied stress to a value below the yield strength of austenite. Any plastic deformation can complicate interpretation because the resulting defect structure can either assist or interfere with the progress of transformation. Published data on the yield strength of austenite as a function of temperature (Fig. 8.3) were extrapolated to estimate its yield strength to be approximately 500 MPa over the temperature range 500–550 °C. Even if the extrapolation is unjustified, the yield strength cannot be less than about 200 MPa, which corresponds to experimental data from 750 °C (Fig. 8.3). Consequently, the experiments were carried out at two load levels, both of which should be well below the austenite yield strength at $T_2$: the chosen loads correspond to stress levels of 116 and 174 MPa. The results of these experiments should be compared against transformation without the influence of any applied stress. However, under the conditions of the experiments, the longitudinal strain cannot be recorded unless a small stress of about 12 MPa is applied, since the cross head uses this signal to follow the dimensional changes in that direction. Consequently, the “zero stress” experiments described here in fact were carried out with the 12 MPa stress during transformation. The details of the actual experiments are listed in Table 8.2; the calculated time–temperature–transformation diagram presented in Fig. 6.1 (for alloy 77) confirms that the transformation temperatures are chosen to first cause the growth of allotriomorphic ferrite and then of acicular ferrite.
Table 8.2 Heat Treatment Schedule of the experiments. In each case the austenitisation heat treatment was carried out at 1150 °C for 10 minutes. The stress was applied immediately after the sample reached $T_2$. $t_1$ and $t_2$ are the time periods spent by the sample at the temperatures $T_1$ and $T_2$ respectively. The prefix "ST" on the specimen identification indicates transformation under the influence of a large stress which is nevertheless below the yield strength of the austenite and "NST" corresponds to the no stress experiment (see text).

<table>
<thead>
<tr>
<th>Identification</th>
<th>$T_1$ °C/ $t_1$ s</th>
<th>$T_2$ °C/ $t_2$ s</th>
<th>Stress MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>NST0</td>
<td>660 / 120</td>
<td>530 / 300</td>
<td>12</td>
</tr>
<tr>
<td>NST1</td>
<td>660 / 120</td>
<td>500 / 300</td>
<td>12</td>
</tr>
<tr>
<td>NST2</td>
<td>660 / 120</td>
<td>500 / 300</td>
<td>12</td>
</tr>
<tr>
<td>ST1</td>
<td>660 / 60</td>
<td>530 / 300</td>
<td>116</td>
</tr>
<tr>
<td>ST2</td>
<td>660 / 120</td>
<td>530 / 300</td>
<td>116</td>
</tr>
<tr>
<td>ST3</td>
<td>660 / 120</td>
<td>530 / 300</td>
<td>174</td>
</tr>
<tr>
<td>ST4</td>
<td>660 / 120</td>
<td>500 / 300</td>
<td>116</td>
</tr>
</tbody>
</table>

8.3 Results and Discussion

8.3.1 The Microstructure

Throughout these experiments, it was our aim to demonstrate a clear effect of stress. The clarity of microstructural changes can be maximised by only partially transforming the austenite to acicular ferrite, and allowing the remainder to decompose by a martensitic transformation during the quench to ambient temperature. Two transformation temperatures were therefore studied, both quite close to the calculated $B_S$ temperature (546 °C). This ensures that the amount of acicular ferrite that forms is limited, because that amount increases from zero at $B_S$ to a quantity determined by the $T'_0$ curve of the phase diagram as the temperature is reduced below $B_S$.

Specimens NST0 and NST1 which are from the zero stress experiments showed similar microstructures, NST1 having a larger quantity of acicular ferrite, as expected from its lower $T_2$ transformation temperature. The microstructure of NST1 is illustrated in Fig. 8.4a. It reveals the thin continuous layer of allotriomorphic ferrite which grew and covered the austenite grain boundaries at $T_1$; in addition, there is the intragranularly nucleated acicular ferrite which formed at $T_2$. The acicular ferrite microstructure is as expected in normal welds, with plates pointing along many directions. Sample NST2 represents a repeat of the treatment given to
NST1. It was used for confirmation of the experimental method during the initial work when the experimental scheme was being designed. Its microstructure was found to be identical to that of NST1.

Fig. 8.4b–e are longitudinal sections of samples ST1–4; the direction of the applied stress is indicated on each of the micrographs. All of these experiments reveal a dramatic change in the microstructure when the acicular ferrite forms under the influence of the applied stress. The number of crystallographic variants per grain is reduced drastically and there is a strong tendency for the plates that do grow to align within any given prior austenite grain.

These results are easily understood once it is accepted that acicular ferrite growth leads to an invariant–plane strain (IPS) change in the transformed region (Strangwood and Bhadeshia, 1987a). A uniaxial compressive stress will oppose the dilatational component of this IPS (Patel and Cohen, 1953), but the shear component will interact favourably. Since the shear component is much larger than the dilatational strain, the overall interaction of the shape change with the strain can be favourable. The compressive stress resolves to give maximum shear stresses on planes which lie at 45° to the stress axis. Given that the samples used are polycrystalline, it is only by fortuitous circumstance that the crystallographic orientation of a particular austenite grain permits acicular ferrite to form on these planes of maximum shear stress. Nevertheless, acicular ferrite variants which happen to be most parallel to those planes are expected to be favoured by the stress, and will form preferentially. This is what leads to the development of the aligned microstructure illustrated in Fig. 8.4b–e. It is noteworthy that there are in principle up to 24 different crystallographic variants of acicular ferrite possible within each austenite grain. Of these, it is likely that one or more may lie fairly close to the 45° orientation. Indeed, it is easy to see from Fig. 8.4b–e that the acicular ferrite plates that grow tend to lie fairly close to the optimum orientation.†

One further observation is relevant; Fig. 8.5 shows higher magnification images of samples NST1 and ST2. It is evident that acicular ferrite tends not to form in the regions of austenite adjacent to the allotriomorphs of ferrite. This is exactly as predicted by theory, that the partitioning of carbon during the growth of the allotriomorphs enriches the adjacent austenite which consequently becomes more stable to transformation when compared with unaffected austenite.

8.3.2 The Transformation Strains

Given the nature of the invariant–plane strain shape change (Fig. 8.1), the transformation strain can only be isotropic if the effects of many different randomly orientation crystallographic

† In fact, although the plane of maximum shear stress is at 45 degrees to the stress axis, the most favoured plane is calculated by also taking into account the dilatational component of the IPS. However, since that component is rather small, 45 degrees is a good approximation for the optimum orientation.
variants are averaged. The shear components would then tend to cancel out, and the dilatational component of the shape change would appear to be like a uniform volume expansion instead of a uniaxial strain normal to the habit plane. This kind of behaviour might be expected in a random, fine grained polycrystalline sample of austenite.

However, if the sample is crystallographically textured, or if the variants do not form at random, then the transformation strain cannot be isotropic, and the net strain along any particular direction may contain contributions from both the shear and dilatational terms. It then becomes possible to detect transformation plasticity as well as volume change.

The strain measurements are presented in Fig. 8.6. In the absence of stress or crystallographic texture, both the longitudinal and radial strains are expected to be positive since only the volume change is detected. As is seen from 8.6, this is true during the initial stages of transformation (NST1, NST2), but not in the later stages, probably because of the small stress of 12 MPa used for these samples, but possibly also because of crystallographic texture in the samples.

For all other samples (ST1-4), the longitudinal strain is always negative as the specimen transforms in a manner which tends to accommodate the applied compressive stress, whereas the radial strains are all positive. The experiments provide impressive proof of the shape deformation accompanying the displacive growth of acicular ferrite. It would be impossible to explain both the magnitude and signs of the strains detected on the basis of a reconstructive transformation mechanism.

More detailed interpretations of these data require methods of accurately deconvoluting the measured strains into the volume change and transformation plasticity terms. That problem is currently under investigation.

8.4 Conclusions

It is found that the acicular ferrite microstructure responds to stresses below the yield strength of the austenite. The response is in fact quite remarkable, the stress favouring the development of specific crystallographic variants. This leads to a destruction of the conventional acicular ferrite structure in which the plates emanating from inclusions point in many different directions. Apart from these microstructural changes, the measured strains during transformation under the influence of stress give conclusive proof for the shape deformation and displacive mechanism of acicular ferrite growth.
Fig. 8.1 Schematic explanation of shape changes due to isotropic volume change and a general invariant plane strain. The invariant plane strain in austenite to displacive ferrite products involve shear and a dilatational component (Bhadeshia et al., 1991).
Fig. 8.2 Schematic illustration of two stage heat treatment schedule for generating acicular ferrite microstructure.

Fig. 8.3 Variation of yield strength as a function of temperature. The graph also contains two extrapolation curves in estimating the yield strength of austenite at around 500 - 550 °C. The experimental data points are for a Nb-V microalloyed steel (Weiss et al., 1981).
Fig. 8.4 Microstructure observed in no stress experiments and stressed samples. For each case there are two microstructures corresponding to the transverse and longitudinal directions. The arrows in the longitudinal section micrographs indicate the stress direction. The details and the heat treatments are given in the Table 8.2: (a) NST1.
Fig. 8.4 continued...

(b) ST1.
Fig. 8.4 continued...

(c) ST2,
Fig. 8.4 continued...

(d) ST3.
Fig. 8.4 continued...

(e) ST4
Fig. 8.5 Microstructure of (a) NST1 and (b) ST2 at higher magnification. The micrograph illustrates the transformation free zone around the allotriomorphic ferrite interface.
Fig. 8.6 Plot of transformation strain in the longitudinal and transverse directions as a function of time for all the experiments listed in Table 8.4. Here the letter 'R' represents the diametral strain $\Delta R$ and 'L' represents longitudinal strain $\Delta L$. 
Chapter 9

Effect of Cobalt on Fe-Cr-Mo-C Weld Deposits

9.1 Introduction

The present research project was initiated to explain the transition from acicular ferrite to bainite in Fe-Cr-C welds. The introduction of thin allotriomorphic ferrite layers on the austenite grain boundaries has been demonstrated to optimise the opportunity for the formation of acicular ferrite ( chapters 4, 5 & 6). The problem with the 2.25Cr-1Mo (wt.% ) welds widely used in industry is that it is important to cool them at rates which allow the formation of allotriomorphic ferrite. The aim of the work presented in this chapter was to introduce the formation of allotriomorphic ferrite by appropriate alloying. Suitable alloying additions are Al, Si and Co, all of which reduce the stability of austenite (Aaronson and Domain, 1966). Silicon is not, however, desirable from the toughness point of view, whereas a large concentration of aluminium cannot be transferred across the welding arc because of its strong oxidising potential. Consequently, cobalt was chosen to reduce the hardenability.

9.2 Design of Welds

The weld microstructure model developed by Bhadeshia et al., (1985), as introduced in chapter 1, is based on the paraequilibrium thermodynamics for the calculation of phase diagrams and TTT diagrams. The alloying additions bring about the change in thermodynamics by:

1. The free energy for transformation from austenite to ferrite in alloyed iron, namely $\Delta G_{Fe}^{\gamma\rightarrow\alpha}$ is modified. The alloying additions modify the magnetic and non magnetic component of free energy vs temperature curves, a concept due to Zener (1955).

2. The carbon activity in austenite is influenced by substitutional alloying additions and this is accounted for, by altering the pairwise carbon-carbon interaction energy ($\omega_c$) in austenite. Aaronson et al., (1966b) represented the free energy change for the austenite Fe-X alloy transforming to ferrite with the same composition by the following equation (Bhadeshia, 1982a):

$$\Delta G_{Fe}^{\gamma\rightarrow\alpha} = \Delta G_{Fe}^{\gamma\rightarrow\alpha}(T - 100 \sum_{i=1}^{n} Y_i(\Delta T_{mag})_i) + 141 \sum_{i=1}^{n} Y_i(\Delta T_{mag} - \Delta T_{non_mag})_i \quad (9.1)$$

Here the curly brackets represent a functional relation. $\Delta T_{mag}, \Delta T_{non_mag}$ are the displacements in the temperature at which the respective free energy change accompanying austenite to ferrite in pure iron are calculated, in order to account for the changes in magnetic and non magnetic free energy components. The values of $(\Delta T_{mag})_i$ and $(\Delta T_{non_mag})_i$ tabulated in the work of
Table 9.1. The magnitudes of $\Delta T_{\text{non.magnetic}}$ & $\Delta T_{\text{magnetic}}$ for various substitutional alloying additions.

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Delta T_{\text{non.magnetic}}$ °C per at. % X</th>
<th>$\Delta T_{\text{magnetic}}$ °C per at. % X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.0</td>
<td>-3.0</td>
</tr>
<tr>
<td>Mn</td>
<td>-39.5</td>
<td>-37.5</td>
</tr>
<tr>
<td>Ni</td>
<td>-18.0</td>
<td>-6.0</td>
</tr>
<tr>
<td>Mo</td>
<td>-17.0</td>
<td>-26.0</td>
</tr>
<tr>
<td>Cr</td>
<td>-18.0</td>
<td>-19.0</td>
</tr>
<tr>
<td>V</td>
<td>-32.0</td>
<td>-44.0</td>
</tr>
<tr>
<td>Co</td>
<td>16.0</td>
<td>19.5</td>
</tr>
<tr>
<td>Cu</td>
<td>-11.5</td>
<td>-4.5</td>
</tr>
<tr>
<td>Al</td>
<td>+15.0</td>
<td>8.0</td>
</tr>
<tr>
<td>W</td>
<td>-17.0</td>
<td>-26.0</td>
</tr>
</tbody>
</table>

Zener (1955) and Aaronson et al., (1966b) were taken for the calculations (Table 9.1) and $Y_i$ is the mole fraction of $i$th substitutional alloying addition disregarding the presence of carbon.

The alloying elements affect the carbon-carbon ($\omega_\gamma$) interaction energies in the austenite, which modifies the activity of carbon. The variations of $\omega_\gamma$ with atom fractions of substitutional alloying elements can be calculated as presented in the references (Aaronson et al., 1966b, Bhadeshia, 1981c) and were represented as a polynomial equation. The variation of $\omega_\gamma$ with atom fraction of cobalt derived by Bhadeshia (1981c) was adopted to present calculations (Figure 9.1).

The model after the above modification predicted a shift of reconstructive transformation to allotriomorphic ferrite to a shorter times, as seen in TTT diagrams. The TTT diagrams will be presented later, together with measured data. The cobalt containing alloy (AM1, 4.3 wt.% Co) was compared with one without cobalt (A1).

9.3 Experimentation

The procedure for all-weld metal test pieces has been explained in chapter 2. The welding variables and detailed weld compositions (A1 - 0.0 wt.% Co and AM1 - 4.3 wt.% Co) are presented in Tables 2.1 & 2.2. The columnar austenite grain sizes ($L_{\text{ctn}}$) were measured and were found to be $105 \pm 21$ and $95 \pm 15 \mu m$. This difference was considered to be insignificant. The austenitisation conditions were 1150 °Cand 10 minutes during dilatometry. The prior austenite grain size after this austenitisation treatment was found to be 80-90 μm. The isothermal
treatments were carried out at 820, 800, 775, 750, 725, 700, 675, 650, 625, 600, 575, and 550 °C for time periods up to one hour.

9.4 Results and Discussion

Figures 9.2 & 9.3 show the absence of allotriomorphic ferrite and acicular ferrite in both alloys with no discernible difference in microstructure. Only bainitic sheaves could be found. The transformation temperatures for the two alloys are presented in Table 9.2. They are, as expected, higher for alloy AM1 compared with A1. Hence, with a similar cooling rate, AM1 might have a tendency to develop into higher volume fractions of martensite. The optical microstructure showed no obvious difference between A1 and AM1. The cobalt thus proved to be ineffective.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>$W_s$ range</th>
<th>$B_s$</th>
<th>$M_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>°C</td>
<td>°C</td>
</tr>
<tr>
<td>A1</td>
<td>660-680</td>
<td>555</td>
<td>440</td>
</tr>
<tr>
<td>AM1</td>
<td>660-780</td>
<td>644</td>
<td>536</td>
</tr>
</tbody>
</table>

Table 9.2. Calculated transformation temperatures for alloy A1 and AM1.

The hardness values in the weld metal regions were found to be 283 ± 6 HV in alloy A1 and 289 ± 6 HV in alloy AM1. Isothermal dilatometric data were compared with the calculated TTT diagrams (Fig. 9.4). The transformation times for a constant volume fraction of transformation (observed from the relative length change) were measured to construct the TTT diagrams. There is negligible difference between the experimental transformation start times of alloy A1 and AM1 for all transformation temperatures above 660 °C. This is consistent with the absence of allotriomorphic ferrite reaction in both welds. The comparison of the experimental and calculated transformation start times for alloy A1 show a good correlation, but, a gross underestimation of the incubation time for cobalt (alloy AM1) containing alloy is evident from Fig. 9.4. The thermodynamic model predicts a order of magnitude smaller incubation time.

If the cobalt addition causes a change in the free energy of transformation, there should be corresponding change in transformation temperature. The bainitic transformation temperatures were measured during continuous cooling at 30 °Cs⁻¹ (Fig. 9.5). The results agree well with the calculations (Bhadreshia, 1982a): A1; Predicted $B_s = 555$, Measured $B_s = 580$ & AM1; Predicted $B_s = 644$, Measured $B_s = 630$ °C. This proves that the cobalt certainly has a thermodynamic effect on bainite.
As a further check, the martensitic transformation temperatures data given by Raghavan and Thomas (1971) were examined with the present thermodynamic model. They studied Fe-0.3C-4Cr (wt.%) with differing cobalt concentration. Their measured $M_s$ temperatures are 348, 333 and 390 °C for cobalt concentrations 0, 1.4, and 5.3 wt.% respectively. Corresponding calculated martensitic transformation temperatures were 325, 383 and 435 °C. The trends are therefore correctly predicted although the discrepancy is large at high concentration. The excellent correlation in the calculated bainitic transformation temperature with the experimental points, and good correlation of TTT data points with experimental points of alloy A1 indicates that the free energy modification was indeed taken into account in the thermodynamic model. Further experiments (Fig. 9.6 and 9.7) verified that cobalt did not accelerate the transformation to allotriomorphic ferrite in Fe-Cr-Mo-C steels.

9.5 Summary

The driving force for transformation is increased on addition of cobalt as indicated by the changes in bainite transformation temperatures, although for reasons which are not clear, it was found not to influence the formation of allotriomorphic ferrite in the alloys studied.
Fig. 9.1 Variation of carbon-carbon ($\omega_\gamma$) interaction energy in austenite as a function of cobalt concentration (after Bhadeshia, 1981c).
Fig. 9.2 Microstructure observed in welds A1 and AM1. The absence of grain boundary nucleated allotriomorph ferrite and acicular ferrite is noticeable. (a) A1, (b) AM1.
Fig. 9.3 Comparison of the primary weld metal microstructures of alloy A1 and alloy AM1. (a) A1, (b) AM1.
Fig. 9.4 Comparison of calculated TTT curves for alloys A1 and AM1. The points were measured using dilatometry. The open circles are for weld A1 and filled circles for weld AM1. Note the similarity of the TTT curves at transformation temperatures above 660 °C for both alloys.
Fig. 9.5 Relative length change as a function of temperature for alloys A1 and AM1. The solid line is $d(\Delta L)/d(T)$ vs $T$. The Dotted lines correspond to the original $\Delta L$ vs $T$. The onset of bainitic transformation is marked with the arrow (a) A1, (b) AM1.
Fig. 9.6 Allotriomorphic ferrite kinetics for the alloys A1 and AM1, for two transformation temperatures, (a) 750 °C, (b) 725 °C.
Fig. 9.7 Corresponding microstructures for the transformation conditions of Fig. 9.6. (a) 750 °C, (b) 725 °C.
Chapter 10

Future Research

The present research has illustrated a simple way of rendering the austenite grain boundaries ineffective in nucleating bainite by decorating them with thin layers of allotriomorphic ferrite. This allows the inclusions within the residual austenite an opportunity to nucleate acicular ferrite. The inertness of allotriomorphic ferrite is explained on the basis of crystallography and solute partitioning.

The columnar austenite grain parameters in weld control the subsequent microstructure development. In single run welds the grain size is controlled by weld composition and the base plate texture. In multirun weld it is further complicated by the solidification segregation patterns created by previous weld passes. Hence, a fundamental model has to be developed using solidification theories, crystallography and thermodynamics of the transformation to $\delta$ ferrite and austenite from liquid steel.

The allotriomorphic ferrite model now needs to be improved to predict crucial parameters such as the extent to which the austenite grain boundaries are covered by layers of allotriomorphic ferrite and the transition from local to para-equilibrium mode of growth. This will require a detailed and extensive re-examination of allotriomorphic ferrite kinetics in both the nucleation and growth stages. The kinetic model should include isothermal and anisothermal transformation conditions.

The second and most promising need is to model the kinetics of transformations under the influence of stress. Further stress/crystallography data ha to be collected, data of importance in variant selection and hence in calculating mechanical driving force. The measured transformation strains with stress will form a basis for calculating the residual stress in welds as they cool. Alloy modification or a change in weld cooling rate conditions can be considered to modify the residual stress development. The application of this research lies in the design of welded joint of high strength steels, which experience thermal, applied and shrinkage stresses.
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