# WIDMANSTÄTTEN FERRITE AND BAINITE IN ULTRA HIGH STRENGTH STEELS

By

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 $\diamondsuit$  To Farhan, Hina, Nida and Faizan

"Science means simply the aggregate of the recipes that are always successful. All the rest is litrature"

Paul Valŕy [1871-1945]

Analects vol. 14 of Collected Works ed. J. Matthews, 1970 (London: Routledge & Kegan Paul)

### PREFACE

This dissertation is submitted for the degree of Doctor of Philosophy at the University of Cambridge. It describes research carried out in the Department of Materials Science & Metallurgy between January 1987 and January 1991, under the supervision of Dr. H. K. D. H. Bhadeshia. 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.

Ashraf Ali

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#### ABSTRACT

The microstructural, thermodynamic and kinetic aspects of Widmanstätten ferrite and bainite in steels have been studied with the aim of providing a better understanding of the mechanisms of phase transformation. The thesis begins with a review of the published literature on the physical metallurgy of steels, concentrating whenever possible, on the aspects important in the modelling of microstructures. This is followed by an experimental study of bainite in steels where the precipitation of carbides is sluggish. The results confirm the hypothesis that bainite grows without diffusion, although any excess carbon in the bainitic ferrite subsequently partitioned into the residual austenite.

The tempering of mixed microstructures of bainitic ferrite and austenite was found to cause changes in the shape of the originally lenticular bainite platelets, towards a more rounded microstructure. Prolonged annealing also led to the coalescence of adjacent platelets, until the austenite decomposed into cementite and ferrite. In steels with molybdenum, the cementite eventually transformed to alloy carbides.

Controlled experiments designed to classify the contradictory published data confirmed that the rate of bainite transformation increases as austenite grain size is reduced. Some spectacular microstructures of commercial significance were generated by decorating the austenite grain surfaces with thin layers of allotriomorphic ferrite in order to force the intragranular nucleation of Widmanstätten ferrite or bainite on minute quantities of oxide particles.

The process of Widmanstätten ferrite nucleation was studied using thermodynamic and kinetic modelling; both new experimental data and the analysis of published results indicate a displacive mechanism in which carbon redistributes during both nucleation and growth. On the other hand, the growth of bainite sheaves appears to occur at a rate much faster then expected from diffusion-controlled growth theory. This, and other experiments on the reverse transformation of bainitic ferrite into austenite, have all been found to be consistent with the model in which bainite is said to grow by a diffusionless mechanism.

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## NOMENCLATURE AND ABBREVIATIONS

$Ae_3$	Upper temperature limit of the $\alpha + \gamma$ phase field at equilibrium					
$Ae'_3$	Upper temperature limit of the $\alpha + \gamma$ phase field at paraequilibrium					
$Ae_1$	Lower temperature limit of the $\alpha + \gamma$ phase field at paraequilibrium					
$Ae'_1$	Lower temperature limit of the $\alpha + \gamma$ phase field at equilibrium					
$a_{Fe}^{lpha}$	Activity of iron in ferrite.					
$a_{Fe}^{\gamma}$	Activity of iron in austenite					
α	Ferrite					
$\alpha_a$	Allotriomorphic ferrite					
$\alpha_b$	Bainitic ferrite					
$\alpha_w$	Widmanstätten ferrite					
$\alpha'$	Martensite					
$a_{\gamma_o}$	Lattice parameter of austenite at the reaction temperature before the					
	reaction, Å					
$a_{\gamma}$	Lattice parameter of austenite at the reaction temperature at any					
	stage of the reaction, Å					
$a_{\alpha_o}$	Lattice parameter of ferrite at ambient temperature (25 $^o\mathrm{C}),$ Å					
$a_{\alpha}$	Lattice parameter of ferrite at reaction temperature, Å					
$B_S$	The temperature at which bain ite first observed to form, in $^o\mathrm{C}$					
$\overline{D}$	Weighted average diffusivity of carbon in austenite					
$E^{str}$	Strain energy per unit volume					
$e_{lpha,\gamma}$	Linear thermal expansion coefficient of ferrite and austenite					
	respectively, $^{o}C^{-1}$					
$G_1$	Stored energy of Widmanstätten ferrite <i>i.e.</i> , 50 J mol <sup><math>-1</math></sup>					
$G_2$	Stored energy of bainite <i>i.e.</i> , 400 J mol <sup><math>-1</math></sup>					
$G_{max}$	Maximum free energy required for the nucleation of					
	Widmanstätten ferrite in J $mol^{-1}$					
$\Delta G^{\gamma \to \gamma' + \alpha}$	Driving force required for the ferrite from austenite					
	with shear in $J \mod^{-1}$					
$\Delta G$	Change in Gibb's free energy, J mol <sup><math>-1</math></sup> K <sup><math>-1</math></sup>					
$G_N$	Minimum amount of free energy required for the nucleation of					
	Widmanstätten ferrite irrespective of the chemical composition					
	of steels in $J \mod^{-1}$					
$\Delta G^{\gamma \to \alpha_s}$	Free energy change accompanying the formation of ferrite in J $mol^{-1}$					
	with the same carbon content as austenite in J $mol^{-1}$					

$\Delta G^{\gamma \to \alpha}$	Free energy change from austenite to ferrite transformation
	in pure iron, in $J \mod^{-1}$
$\Delta G_o^*$	Activation energy in the absence of applied stress
$\Delta G^{chem}$	Chemical driving force, $J \mod^{-1}$
$\Delta G^*$	Activation energy term of isothermal nucleation theory in J $\mathrm{mol}^{-1}\mathrm{K}^{-1}$
$\Delta G_v^o$	Maximum volume free energy change accompanying the formation
	of nucleus in a large amount of matrix phase in J $mol^{-1}K^{-1}$
IPS	Invariant plane strain
L	Length of the specimen prior to the transformation, mm
$\Delta L$	Length change due to transformation, mm
$M_S$	Martensite start temperature, in $^{o}C$
N	Steady state nucleation rate
NP-LE	Negligible partitioning local equilibrium
P-LE	Partitioning local equilibrium
$V_{\alpha}$	Volume fraction of ferrite transformed
$\gamma$	Austenite
$T_{\gamma}$	Isothermal reaustenitisation temperature in $^{o}C$
σ	Interfacial energy per unit area
$T_0$	Temperature at which stress-free austenite and ferrite of the same
	composition have identical free energies, $^{o}C$
$T'_0$	Same as $T_0$ except taking stored energy 400 J mol^{-1} of bain ite, $^o\mathrm{C}$
r	Radius of spherical nucleus
$r^*$	Radius of critical nucleus
R	Universal gas constant
S	Carbon locked up in ferrite, at. $\%$
T	Reaction temperature in <sup>o</sup> C
$\tau_s$	Incubation period, s
$\tau_o$	Shear stress required to move an array of n dislocations
ν	Pre-exponential attempt frequency factor of nucleation theory
$\rho_A$	Density of atoms in the closed packed plane
$\overline{x}$	Average carbon content in the steel, at. %,
$x_{Si}$	Average silicon content in the steel, at. $\%$
$x_{Mn}$	Average manganese content in the steel, at. $\%$
$x_{Mo}$	Average molybdenum content in the steel, at. $\%$
$x_{\gamma}$	Carbon content of residual austenite at any stage of the reaction, at. %
$\overline{x}$	Average carbon concentration of the alloy

$x_{max}$	Maximum level of carbon permitted in ferrite for a specified carbon
	concentration in the austenite at the interface
$x^{\gamma \alpha}$	Equilibrium concentration of carbon in austenite at
	austenite/ferrite interface
$x^{\alpha\gamma}$	Equilibrium concentration of carbon in ferrite at
	austenite/ferrite interface
$W_S$	The highest temperature at which Widmanstätten ferrite forms in a
	detectable amount, in <sup>o</sup> C

There is a complex series of reconstructive and displacive transformation products formed as a result of the decomposition of austenite during transformation at temperatures below  $Ae_3$ , when various alloying elements are added to pure iron. These microstructures vary not just in morphology, but in phase composition, structure and thermodynamic stability. The microstructure of low-alloy steels can contain allotriomorphic ferrite, Widmanstätten ferrite, acicular ferrite, bainite, martensite and retained austenite, depending upon the transformation temperature, alloy composition and cooling rate etc.

The austenite to ferrite  $(\gamma \rightarrow \alpha)$  transformation in low-alloy steels is a topic of vital concern to metallurgists and considerable attention has been given in recent years to the elucidation of the mechanisms which govern the displacive decomposition of austenite to ferrite [Bhadeshia, 1981a; 1987a].

In the following section some of the basic concepts which govern the displacive transformation mechanism are discussed. A comparative study of the reconstructive and displacive transformation mechanisms is presented and finally, various decomposition products formed by both reconstructive and displacive transformation mechanisms are described.

### 1.1 Reconstructive, Martensitic and Displacive Transformations

Based on the features exhibited by a transformation product, such as morphology, chemical composition and change in the shape of the transformed region, the  $\gamma \rightarrow \alpha$  decomposition reaction can be classified into three main groups [Christian, 1975a; Bhadeshia, 1985a]. Reconstructive transformations are those in which the interface advances by the thermally activated uncoordinated movement of atoms across the interface (the atoms behave in the manner of civilians). That is they move independently of each other and in an apparently random manner.

For a reconstructive transformation, it is evident (Fig. 1.1) that the product phase can (although it need not) be of a different composition from the parent phase. In addition, there has been much mixing up of atoms during transformation and there is no atomic correspondence between the parent and product lattices. Because the transformation involves a reconstruction of the parent lattice, atoms are able to diffuse and mix in such a way that the invariant-plane strain (IPS) shape



Fig. 1.1: Schematic illustration of the mechanism of reconstructive and martensitic transformations in a substitutionally alloyed materials. The lines joining "atoms" connects corresponding direction of the parent and product lattices [Bhadeshia, 1987b].

deformation (and its attendant strain energy) does not arise. The diffusion necessary to accomplish the lattice change without the strain accompanying the coordinated movement of atoms is called *reconstructive diffusion* [Bhadeshia, 1985a], and it is necessary even when reconstructive reactions occur in a pure element. Reconstructive transformations can be regarded as simultaneous transformation and recrystallisation, the recrystallisation part involving reconstructive diffusion.

Martensitic or military transformations are reactions in which the rearrangement of atoms takes place in an orderly, disciplined manner, the transfer being diffusionless. Since the pattern in which the atoms of the parent crystal arranged nevertheless changes in a way that is consistent with the change in crystal structure, it follows that there must be a physical change in the macroscopic shape of the parent crystal during transformation. This shape change in the transformed region can be observed, if a pre-polished specimen is allowed to transform to a martensitic transformation. This particular shape change is known as *invariant-plane strain*§, and it has a shear component as well as with the dilatation component [Christian, 1958]. Fig. 1.1 shows that in a martensitic transformation, labelled rows of atoms in the parent crystal remain in the correct sequence in the martensite lattice, despite transformation. As there is no mixing up of atoms during transformation, it is possible to suggest that a particular atom of the martensite originated from a corresponding particular atom in the parent crystal. This property may be expressed by stating that there exists an atomic correspondence between the parent and product lattices.

In interstitially alloyed materials, the substitutional lattice can transform without diffusion while the interstitials may diffuse [Christian, 1962], this is *displacive transformation*. The diffusion of interstitials has no influence on the shape change accompanying transformation so that the macroscopic characteristics of martensite are retained. Only a partial atomic correspondence (between atoms on the substitutional lattices) exists between the parent and product lattices. Martensitic transformations can be regarded as a *diffusionless* subset of displacive transformations [Cohen *et al.* 1979].

#### 1.2 Comparison between Martensitic and Displacive Transformations

Martensitic reactions are always interface-controlled whereas displacive or reconstructive transformations need not be; their rate can be controlled by diffusion

 $<sup>\</sup>S$  see also section 1.6 for details.

in the parent phase. In both displacive and martensitic transformations, the product phase always has thin-plate morphology since this minimizes the strain energy associated with the shape deformation [Bilby and Christian, 1956].

In martensitic or displacive transformations the structure of the interface necessarily has to be coherent or semi-coherent in order to ensure glissile interfaces. The kinetics, however may be controlled by either the nucleation or the growth rate. The experimental criterion which best distinguishes between martensitic or displacive transformations from reconstructive transformations is the observation of whether or not there is an IPS change of shape with a significant shear component, in the transformed region [Bilby and Christian, 1956]. Table 1.1 shows a comparison of the characteristics of all the three types of transformations.

Table 1.1: Comparison of reconstructive, displacive and martensitic transformations (adapted from Bhadeshia, [1987a]).

Characteristic/Feature	Transformation Product					
	Reconstructive	Martensitic	Displacive			
Diffusion of substitutional						
alloying elements	yes	no	no			
Diffusion of interstitial						
alloying elements	yes	no	no			
Atomic correspondence						
between the parent						
and product phases	nil	yes	yes			
Movement of atoms	random	coordinated	coordinated			
Morphology	not particular	plate or lath	plate or lath			
IPS shape change	nil	yes	yes			
Composition of the	equilibrium or	same as	equilibrium or			
product phase	paraequilibrium	parent phase	paraequilibrium			
Rational orientation			÷			
with parent austenite	no	yes	yes			
Can cross prior austenite						
grain boundaries?	yes	no	no			

#### **1.3 Interface Structures**

The  $\gamma \to \alpha$  transformation is a first order transformation  $\S$ , which occurs by the

DISPLACIVE PHASE TRANSFORMATIONS

<sup>§</sup> In second order transformations the parent and product phases do not coexist and there is no identifiable interface. The transformation happens in all regions of the parent phase.

motion of well defined interfaces. The structure of the interfaces influences the way in which the atoms of the parent lattice move in order to generate the  $\alpha$  lattice. The interfaces may be divided into fully coherent, semi coherent, and incoherent interfaces [Chadwick, 1972; Bruke, 1965].

#### 1.3.1 Fully Coherent Interfaces

A fully coherent interface arises when the two crystals match perfectly at the interface plane, so that the two lattices are continuous across the interface (Fig. 1.2a). This can only be achieved if, disregarding chemical species, the interfacial plane has same atomic configuration in both phases i.e., rows and planes of atoms are continuous across this interface and this requires the two crystals to be orientated relative to each other in a special way. A twin boundary in a single phase material is an example of a perfectly coherent boundary.

When the distance between the atoms in the interface is not identical it is still possible to maintain coherency by straining one or both of the two lattices as illustrated in Fig. 1.2b. The resultant lattice distortions are known as coherency strains. If these strains are not too large they can be accommodated by dilatation in the plane of the interface.

In the situation when the two lattices match perfectly at the interface, the surface energy between precipitate and lattice is virtually nil, making the nucleation barrier small. However, if the equilibrium (stress free) lattice parameters of the solute-rich phase and the matrix differ, the precipitate will be strained so that the  $E^{str}$  is always positive.

The coherent interfaces imply a definite orientation relationship between the precipitate lattice and the matrix.

#### 1.3.2 Semi-Coherent Interface

A semi-coherent interface may be regarded as an interface in which regions of coherency are separated by regions of discontinuity (Fig. 1.2b). The structures do not really fit at the interface, and the mismatch would accumulate unless periodically corrected. There are two kinds of semi-coherency [Christian, 1975b]: i) glissile interfaces and ii) epitaxial semi-coherency.

#### 1.3.2.1 Glissile Interfaces

If the discontinuities discussed above consist of a single set of screw dislocations i.e., when the transformation strain is an invariant-line strain (consisting of the Bain strain and an appropriate rigid body rotation), and the invariant-line lies in

the interface [Christian, 1969], then the latter need only contain a single set of misfit dislocations. For martensitic transformations, the transformation strain has to be an invariant-line strain in order to ensure a glissile interface [Christian, 1969]. A glissile interface also requires that the glide planes (of the misfit dislocations) associated with the  $\alpha$  lattice meet the corresponding glide planes in the  $\gamma$  lattice edge to edge in the interface, along the dislocation lines.



Fig. 1.2: Schematic drawings of the atomic arrangements at interfaces [Chadwick, 1972]. a) Perfectly coherent. b) Elastically strained coherent. c) Semi-coherent. d) Incoherent.

Glissile  $\alpha / \gamma$  interfaces can move conservatively and when they do so, the interface dislocations homogeneously shear the volume of material swept by the interface in such a way that the macroscopic shape change accompanying the transformation is an IPS, even though the homogeneous lattice transformation strain is an invariant-line strain. Conservative motion of a glissile interface leads to martensitic transformation.

### 1.3.2.2 Epitaxial Semi-Coherency

If the intrinsic interface dislocations have Burger's vectors which lie in the interface plane, not parallel to the dislocation line, then the interface is said to be "epitaxially semi-coherent" (Fig. 1.3). The normal displacement of such an interface necessitates the thermally activated climb of the misfit dislocations, so that the interface can only move in a non-conservative manner with relatively restricted mobility at low temperatures.



Fig. 1.3: Diagrammatic illustration of the shape change accompanying the movement of epitaxially semi-coherent interface [Bhadeshia, 1987b].

The nature of the shape change that accompanies the motion of an epitaxially semi-coherent interface is difficult to assess. As discussed by Christian [1975b, 1969], the upward non-conservative motion of the boundary AB (Fig. 1.3) to a new position CD' should change the shape of a region ACDB of the parent crystal to a shape AC' D' B of the product phase. The shape change thus amounts to a uniaxial distortion normal to AB together with a shear component parallel to the interface plane (i.e. an IPS). Because of the dislocations climb in the process, the total number of atoms in the regions ACDB and AC' D' B will not be equal, the difference being removed by diffusion normal to the interface plane. Atomic movements are therefore necessary over a distance (at least) equal to that moved by the boundary, corresponding to the thickness of the transformed region. If this constitutes the only reconstructive flux that accompanies interface motion, then the shear component of the shape change will not be destroyed, and the transformation will exhibit surface relief effects, normally associated with displacive transformations. The mobility will, of course, be limited by the climb process. A situation like this in effect amounts to an orderly diffusion of atoms as the interface migrates (i.e. removal of the extra half-planes of the misfit dislocations) so that a partial atomic correspondence is still maintained between parent and the product phases.

#### **1.3.3** Incoherent Interfaces

As the misfit between adjacent crystals increases, the dislocations in the connecting interface become more closely spaced. They eventually coalesce so that the boundary consists of closely spaced "vacancies" or "dislocation cores". Such a boundary is said to be incoherent; there is a little correlation of atomic positions across the boundary.

In general, incoherent interfaces result when two randomly orientated crystals are joined across any interfacial plane as shown in Fig. 1.2d. They may, however, also exist between crystals with an orientation relationship if the interface has a different structure in the two crystals. They are characterised by a high energy ( $\simeq 0.5$ -1.0 J m<sup>-2</sup>) [Porter and Easterling, 1988], insensitive to the orientation of the interfacial plane.

#### **1.3.4** Interface Mobility

During a phase transformation, one crystal grows at the expense of the other by the migration of the boundary interface. It is clear that if the structures are fully coherent a lattice correspondence is implicit in this process, so that labelled rows or planes of lattice sites in one crystal become rows or planes in the other. The motion of a coherent boundary without diffusion thus produces a macroscopic change of shape which is specified by the relation between the lattices.

In a semi-coherent boundary, since the lattice deformations are not compatible, the motion of the boundary cannot produce a change of shape given by the local atomic correspondence. The shape change produced is obtained by combining the lattice change with the change due to the migration of the discontinuities in the boundary (lattice-invariant deformation). It follows that for both fully coherent and semi-coherent boundaries the shape change produced by motion of the boundary is an invariant-plane strain [Christian, 1975b].

If the boundary is incoherent, there is no correspondence between parent and the product phases and no shape change when it moves. The motion of an incoherent boundary can only cause reconstructive transformations. Thus the growth of a mechanical twin changes the shape of the specimen, but the motion of a general grain boundary or of an annealing twin does not.

Incoherent, coherent and semi-coherent boundaries can coexist around a particle which has grown diffusionally by reconstructive transformation. Only semicoherent and coherent boundaries can exist around a particle which has grown displacively.

#### 1.4 Shape Change Due to Martensitic Transformations

The salient feature of a martensitic transformation is that the transformed region undergoes a change of shape, if a surface of the parent crystal is polished to be flat before the transformation. The nature of the shape deformation in the transformed region has been discussed by Bilby and Christian [1956], and is shown schematically in Fig. 1.4, where a martensite plate LMNOABCD meets a plane surface EFGH. In the region of the plate, the surface is tilted about the lines AB and CD. The surface ABCD remains plane, and a scratch SS' remains continuous and deforms into straight sections STT' S'.

The shape deformation thus deforms planes into planes and straight lines into straight lines; such a deformation is called "homogeneous". It is evident that if cavities are not to appear along the surfaces ABML and DCNO, there can be no rotation of these surfaces as the plate thickens. The experimental observation that the plate and matrix may be kept in focus with a high-powered objective throughout their length shows further that the lines AB cannot be rotated by more than a few minutes of arc. Since the free surface EFGH is arbitrary, it follows that no line

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in the interface ABML (or DCNO) is rotated. It remains possible that there is a contraction or expansion uniform in all directions of these surfaces (a negative or positive dilatation), since this would leave all lines in the surfaces unrotated.

A section through XY shown in Fig. 1.4b, illustrates that there is considerable elastic distortion induced in the matrix around the plate due to the preservation of continuity at the interface. This distortion imposes constraints on the growing crystal and causes it to adopt the form of a lenticular plate, the usual form of martensite crystals.

#### 1.5 Invariant-Plane Strain

If the operation of a strain, leaves one plane of the parent crystal completely unrotated and undistorted; this is known as an invariant-plane strain (IPS). Fig. 1.5, illustrates three such strains. Fig. 1.5a is an example of invariant-plane strain which is purely dilatational, and is of the type to be expected when a plate-shaped precipitate grows reconstructively. This type of IPS reflects the volume changes accompanying the transformation. In Fig. 1.5b, the invariant-plane corresponds to a simple shear, involving no change of volume, as homogeneous deformation of crystal by slip. The shape of the parent crystal alters in a way which reflects the shear character of the deformation. The most general invariant-plane strain (Fig. 1.5c) involves both a volume change and a shear and associated with the martensitic transformations.



Fig. 1.5: Three kinds of invariant-plane strains. The heavy lines indicate the shape before deformation, s,  $\delta$  and md respectively [Bhadeshia, 1987b].

#### 1.6 The Effects of Alloying Elements

The addition of alloying elements to steels affects both the thermodynamics and kinetics of the decomposition of austenite. The aim of this section is to mention briefly how alloying additions influence the transformations. Alloying elements in steel can be classified as substitutional, slow diffusers requiring vacant lattice sites, and interstitial, fast diffusers which occupy the sublattice of interstices, and either or both can control growth rate depending on the driving force. If the local equilibrium is maintained at the  $\alpha/\gamma$  interface, two modes of proeutectoid ferrite growth in an Fe-C-X system (where X is a substitutional alloying element) are possible, depending on alloy composition. These modes are characterized as follows [Coates, 1973]:

#### **1.6.1** Partition-Local Equilibrium (P-LE)

For low supersaturations, X partitions between the ferrite ( $\alpha$ ) and parent austenite ( $\gamma$ ) phase. The flux of carbon is reduced by making the C-concentration gradient very shallow. The precipitate growth rate is low and is determined by the slow diffuser, X, i.e., X exerts a reconstructive drag on the growth kinetics, which is a consequence of the fact that it diffuses many orders of magnitude slower than carbon. Fig. 1.6, shows ferrite growth occurring with local equilibrium at the  $\alpha/\gamma$  interface in Fe-Mn system.

#### **1.6.2** Negligible Partition-Local Equilibrium (NP-LE)

For higher supersaturations, the precipitate growth rate is relatively high and is determined by the fast diffuser, C. In this regime, X, exerts essentially no reconstructive drag effect, in spite of its low diffusivity. The gradient of X is made very steep to increase the flux, by partitioning very little X between  $\gamma$  and  $\alpha$ . A given bulk composition is expected to pass from NP-LE to P-LE regime with increasing temperature. During NP-LE growth, the width of the X concentration spike in  $\gamma$  is a few nanometers. As the temperature of transformation decreases the X concentration spike also decreases until it becomes approximately equal to atomic dimensions. The condition is then reached where the substitutional atoms become configurationally frozen, and equilibrium breaks down at the interface. This constrained equilibrium, in which X is not redistributed during transformation is known as "Para-equilibrium". However, C is still mobile, and subject to the constraint that Fe/Mn ratio is identical in  $\alpha$  and  $\gamma$ , it reaches equilibrium.

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Fig. 1.6: Schematic isothermal sections of the Fe-Mn-C system, illustrating ferrite growth occurring with local equilibrium at the  $\alpha/\gamma$  interface [Bhadeshia, 1985a]. (a) Growth at low supersaturations (P-LE) with bulk redistribution of Mn. (b) Growth at high supersaturations (NP-LE) with negligible partitioning of Mn during transformation. The bulk alloy compositions are designated "A" and "B" in (a) and (b) respectively. c) Division of  $\alpha + \gamma$  phase field into domains where either the P-LE or NP-LE mechanisms can operate.

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### 1.7 Classification of Ferritic Microstructures

The decomposition of the higher temperature face-centered cubic  $\gamma$ -iron to the less dense body-centered cubic allotrope ( $\alpha$ ) gives rise to a variety of different morphologies and microstructures depending upon the cooling rate, presence of alloying elements, the availability of lower energy nucleation sites for heterogeneous nucleation. Thus austenite can decompose into allotriomorphic ferrite, Widmanstätten ferrite, acicular ferrite, bainite, pearlite and martensite. A classification scheme for the products formed by the decomposition of austenite based on the nucleation and growth mechanism is presented in Fig. 1.7.



Fig. 1.7: Classification of transformation products formed by decomposition of austenite according to the nucleation and growth mechanisms.

#### **1.8 Reconstructive Decomposition of Austenite**

Ferrite which grows by a reconstructive transformation mechanism can be classified into two main forms: allotriomorphic ferrite and idiomorphic ferrite.

#### **1.8.1** Allotriomorphic Ferrite

The term "allotriomorphic" means that the phase is crystalline in internal structure but not in outward form. It implies that the limiting surfaces of the crystal are not regular and do not display the symmetry of its internal structure [Bhadeshia, 1985]. The allotriomorphic ferrite (Fig. 1.8a) which nucleates at prior austenite grain boundaries tends to grow along the  $\gamma$ -grain boundaries at a rate faster than in the direction normal to plane, so that its shape is influenced strongly by the presence of the boundary and hence does not necessarily reflect its internal symmetry. Of course, allotriomorphic ferrite need not form just at austenite grain boundaries; but it invariably does so, presumably because there are no other suitable (two-dimensional) heterogeneous nucleation sites in austenite.

The allotriomorphic ferrite grains nucleate at the highest temperatures, i.e. just below  $Ae_3$ , and during the growth stage have a semi-coherent interface with the other adjacent abutting grain. As the transformation temperature is lowered, these crystals develop facets on at least one side of the boundary (Fig. 1.8).

#### 1.8.1.3 Growth of Allotriomorphic Ferrite

The kinetics of allotriomorphic ferrite reaction play an important role in determining the hardenability of steels and also is very important to microstructural predictions as this determines the volume fraction of austenite available to transform into the other phases and the carbon enrichment of the remaining austenite has occurred. A high volume fraction of allotriomorphic ferrite would necessarily limit the amount of austenite left for further different decomposition reactions to follow. Hence any errors in the volume fraction of allotriomorphic ferrite ( $V_{\alpha}$ ) will be magnified throughout the rest of the factors controlling  $V_{\alpha}$ , as the large volume fraction is associated with poor toughness [Levine and Hill, 1977]. The large width of allotriomorphic ferrite allows cracks to develop a large size so that at low temperatures propagation of such defects occurs readily.

The growth of allotriomorphic ferrite  $\alpha$  can be treated in terms of the normal migration of planar  $\gamma/\alpha$  interfaces. It is noted that the growth of  $\alpha$  in dilute steels occurs without the bulk partitioning of substitutional alloying elements [Aaronson and Domain, 1966], especially when the growth rates involved are large [Coates,



(b)

(a)

Fig. 1.8: Optical micrographs showing heterogeneous nucleation of allotriomorphic ferrite at prior austenite grain boundaries and they subsequently grew along these boundaries and growth of allotriomorphic ferrite at prior austenite grain boundaries in Fe-0.22C-2.05Si-3.07Mn-0.7Mo (wt. %) steel austenitised at 1100 °C for 10 min and transformed at (a) 750 °C @ 20 hr (b) 735 °C@ 20 hr.

1973; Glimour *et al.* 1972], as is the case for weld deposits. In these circumstances, ferrite growth can occur at a rate controlled by diffusion of carbon in the austenite ahead of the interface. If it is assumed that the growth of the layer of  $\alpha$  is diffusion-controlled (diffusion of carbon) in austenite, and that for alloy steels the transformation occurs under paraequilibrium conditions [Bhadeshia, 1985], then for isothermal transformation the volume fraction of allotriomorphic ferrite should depend mainly on the parabolic rate constant  $\alpha_1$ ,

$$q = \alpha_1 t^{0.5} \tag{1.1}$$

where q is the half-thickness of the allotriomorphic ferrite layer and t is the time, defined to be zero when q=0. The numerical value of  $\alpha_1$  can obtained by solving the equation [Christian, 1975b],

$$\frac{2(x^{\gamma\alpha} - \overline{x})}{(x^{\gamma\alpha} - x^{\alpha\gamma})} (\frac{\overline{D}}{\pi}) = \alpha_1 [exp(\frac{\alpha_1^2}{4\overline{D}})] [1 - erf(\frac{\alpha_1}{\sqrt{2\overline{D}^{1/2}}})]$$
(1.2)

where  $x^{\gamma\alpha}$  is the paraequilibrium carbon content in the austenite,  $x^{\alpha\gamma}$  is the paraequilibrium carbon content in the ferrite,  $\overline{x}$  is the average carbon concentration of the alloy and  $\overline{D}$  is the weighted average diffusivity of carbon in the austenite [Bhadeshia, 1981b].

#### **1.8.2** Idiomorphic Ferrite

The term idiomorphic implies that the phase concerned has faces belonging to its crystalline form. In steels, idiomorphic ferrite is taken to be that which has a roughly equiaxed morphology (Fig. 1.9). Idiomorphic ferrite usually forms intragranularly [Bhadeshia, 1985], presumably at inclusions or other heterogeneous nucleation sites.

Since both idiomorphic and allotriomorphic ferrite grow by a reconstructive transformation mechanism, their growth is not restricted by austenite boundaries. The extent of penetration into particular grains may vary since interface mobility can change with  $\alpha/\gamma$  orientation relationship.

#### 1.8.3 Massive Ferrite

Massive ferrite, which also grows by a reconstructive transformation mechanism, has the distinction that it inherits the composition of the parent austenite. The ability to cross parent austenite grain boundaries seems particularly pronounced during massive transformation; the final ferrite grain size can be larger than the initial grain size of the austenite. The lack of composition change allows



Fig. 1.9: Formation of idiomorphic ferrite in alloy Fe-0.39C-2.05Si-4.08Ni (wt. %) steel, austenitised at 1300 °C @ 30 min and transformed at 680 °C @ 3hr.



Fig. 1.10: Formation of massive ferrite in alloy Fe-0.05C-2.05Si-4.08Ni (wt. %) steel, austenitised at 1300 °C @ 10 min and transformed at 600 °C @ 60 s.

the transformation to proceed until all of the austenite is consumed. These factors combined to give a single-phase microstructure of larger grains of ferrite which have an approximately equiaxed morphology due to impingement between neighbouring grains as shown in the micrograph of Fig. 1.10.

#### **1.9 Displacive Decomposition of Austenite**

The products resulting from displacive decomposition of austenite can be, Widmanstätten ferrite, bainite, acicular ferrite and martensite, depending upon chemical composition and transformation temperature. The displacive transformation products are very important form engineering point of view, because the volume fraction of these products directly affects the mechanical properties of the steels. For example steels in bainite conditions show a remarkable combination of strength and toughness [Nakasugi *et al.* 1983] and the large volume fraction of acicular ferrite enhances the toughness [Garland and Kirkwood, 1975].

#### 1.9.1 Widmanstätten Ferrite

Widmanstätten ferrite is a phase formed by the transformation of austenite below  $Ae_3$ . It forms in a temperature range where reconstructive transformations become relatively sluggish and give way to displacive transformations. Widmanstätten ferrite which grows by a displacive transformation mechanism, maintains an atomic correspondence between the parent and product phases. On an optical scale, Widmanstätten ferrite has the shape of a thin wedge (Fig. 1.11), the actual shape being somewhere between that of a plate and a lath§.

Widmanstätten ferrite can nucleate either directly from austenite grain boundaries, called "Widmanstätten ferrite primary side plates" or it can nucleate from previously formed grain boundary allotriomorphic ferrite, "Widmanstätten ferrite secondary side plates", both morphologies are shown in Fig. 1.12.

Widmanstätten ferrite  $(\alpha_W)$  formation generally involves the cooperative growth of two mutually accommodating plates. The adjacent plates generally turn out to be similarly orientated, presumably because the simultaneous nucleation of such variants is relatively easy [Bhadeshia, 1981a]. Widmanstätten ferrite forms at low undercoolings below the  $Ae_3$  temperatures, where the driving force for the transformation is small, with an equilibrium or paraequilibrium carbon content.

<sup>§</sup> If a plate or lath is idealized as a rectangular parallelepiped with sides of lengths, a, b, and c then a = b >> c for plate and a >> b >> c for lath [Bhadeshia, 1985].



Fig. 1.11: Optical micrograph showing the classical wedge shape of Widmanstätten ferrite in Fe-0.22C-2.05Si-3.07Mn-0.7Mo (wt. %) steel transformed at 700 °C @ 25 days after austenitisation at 1100 °C @ 10 min.

Since the partitioning of carbon at these temperature is a thermodynamic necessity and since the transformation interface is glissile, the growth of Widmanstätten ferrite is controlled by the diffusion of carbon in the austenite ahead of the interface.

The formation of Widmanstätten ferrite is also accompanied by a change in the shape of the transformed region [Bhadeshia, 1981a; Watson and McDougall, 1973]. The shape change due to a single wedge of Widmanstätten ferrite consists of two adjacent and opposing invariant-plane strain (IPS) deformations [Bhadeshia, 1981a]. These IPS deformations each have a large shear component (0.4) [Watson and McDougall, 1973] and imply the existence of an atomic correspondence between the parent and product phases as far as the iron and substitutional solute atoms are concerned. Interstitial atoms like carbon can diffuse during growth without affecting the shape change or the displacive character of the transformation [Bhadeshia, 1985]. The cooperative growth of a pair of adjacent mutually-accommodating crystallographic variants allows the elastically accommodated strain energy



- 21 -

(a)



Fig. 1.12: Optical micrographs showing various forms of Widmanstätten ferrite in a Fe-0.42C-2.0Si (wt. %) steel. (a) Primary Widmanstätten ferrite formed directly from the prior austenite grain boundaries (1300 °C @ 30 min  $\rightarrow$  680 °C @ 60 s). (b) Secondary Widmanstätten ferrite formed from the allotriomorphic ferrite (1300 °C @ 10 min + 680 °C @ 5 min).

accompanying plate formation to be rather small, of the order of 50 J mol<sup>-1</sup> [Bhadeshia, 1981a]. This is consistent with the low undercoolings at which Widmanstätten ferrite forms and the wedge morphology which arises because the adjacent variants have slightly different habit planes. The shape change indicates that the  $\alpha/\gamma$  interface is glissile and the plates therefore grow at a constant rate controlled by the diffusion of carbon in the austenite ahead of the plate tip. Widmanstätten ferrite cannot be put into the group of reconstructive transformation products, because there is no diffusion involved in the actual lattice change, iron and substitutional elements do not diffuse during transformation. There is no reconstructive diffusion during the formation of Widmanstätten ferrite.

#### 1.9.2 Bainite

Bainite forms by the decomposition of austenite at a higher undercooling relative to Widmanstätten ferrite and grows in the form of sheaves originating from austenite grain boundaries. The sheaf consists of much smaller platelets (sub-units) of ferrite. The sheaf itself has a wedge shaped plate morphology on a macroscopic scale.

When carbon is present, cementite precipitation occurs from the austenite between the sub-units in the case of upper bainite; while in lower bainite, the cementite (or  $\eta$ -carbide) can also precipitate from within the bainitic ferrite.

#### 1.9.2.4 Upper Bainite

Upper bainite consists of platelets of ferrite adjacent to each other, which are in very nearly the same crystallographic orientation in space, so that whenever two adjacent plates touch, a low-angle boundary arises. Elongated cementite particles usually decorate the boundaries of these plates, the amount of these slabs of cementite depending on the carbon content of the steel. These ferrite platelets, which form a sheaf, have the same habit plane [Bhadeshia and Edmonds, 1979]. Sheaves of the upper bainite inevitably nucleate at prior austenite grain boundaries, and intragranular nucleation is not to be found.

The bainitic ferrite after transformation may retain a small supersaturation of carbon, and has a rational orientation relationship with the austenite. In siliconcontaining steels, [Yang and Bhadeshia, 1987], it has been shown that sub-units within a sheaf of upper bainite can also be distinguished where no carbide forms but where the ferrite platelets are separated by films of carbon-enriched austenite (Fig. 1.13).
# 1.9.2.5 Lower Bainite

Lower bainite occurs at a lower temperature compared to upper bainite and is basically very similar to upper bainite, except that the amount of interplate cementite is less, and carbides can additionally be found within the ferrite plate itself. These intra-ferrite carbides can be  $\eta$ -carbides in the case of high carbon steels or cementite in the case of low carbon steels. It has been demonstrated [Yang and Bhadeshia, 1987] that  $\eta$ -carbides will not form in bainitic ferrite for steels with a carbon content below approximately 0.55 wt. %.

The carbide particles usually precipitate in a single crystallographic orientation such that their habit plane is inclined at about 60° to the plate axis. In some cases several variants have been observed [Bhadeshia and Edmonds, 1979], although the 60° variant still tends to dominate. The inter-plate carbide does not necessarily occur and results from the reconstructive decomposition of carbon-enriched austenite which has not transformed to ferrite. Lower bainite also forms as sheaves. A typical microstructure of lower bainite is shown in Fig. 1.14.

In both cases (upper bainite and lower bainite), the formation of a sub-unit is accompanied by an IPS shape change of the transformed region. Fig. 1.15 shows the surface relief accompanied by the formation of bainite. The sub-units within a given sheaf have the same habit plane, orientation relationship with the austenite, and shape deformation.

# 1.9.3 Acicular Ferrite

Acicular ferrite which also grows by a displacive transformation mechanism [Yang and Bhadeshia, 1987] is not included in the Dubé [1948] classification. The morphology of acicular ferrite consists of non-parallel plates of ferrite within the austenite grains, (Fig. 1.16). During the early stages of the transformation, these plates nucleate on inclusions present in the austenite grains. The subsequent plates nucleate sympathetically on these inclusion-nucleated plates. Acicular ferrite is essentially, intragranularly nucleated bainite. The presence of acicular ferrite seems to be directly correlated with the improved toughness [Abson and Pargeter, 1986].



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(b)

(a)

Fig. 1.13: Micrographs showing bainite microstructure in Fe-0.22C-2.05Si-3.07Mn-0.7Mo (wt.%) alloy austenitised at 1000 °C @ 5 min and isothermally transformed at 400 °C @ 2000 s. (a) Optical micrograph. (b) Bright field TEM micrograph.



(a)



(b)

Fig. 1.14: Micrographs showing lower bainite microstructure in Fe-0.43C-2.12Si-3.0Mn (wt.%) alloy austenitised at 1200 °C @ 5 min and isothermally transformed at 246 °C @ 30 min. (a) Optical micrograph. (b) Bright field TEM micrograph (after Bhadeshia and Edmonds, [1979]).



Fig. 1.15: Micrographs showing the surface relief accompanied by the formation of bainite in Fe-0.22C-2.05Si-3.07Mn wt. % alloy. Specimen austenitised at 900 °C @ 5 min and isothermally transformed at 400 °C @ 1000 s. (a) Imaged by Nomarski interference contrast. (b) Same specimen after polishing on 6  $\mu$ m diamond paste and etched.

(a)

(b)



(b)

(a)

Fig. 1.16: Micrographs showing acicular ferrite microstructure. (a) Optical micrograph of specimen from Fe-0.067-0.44Si-1.22Mn-0.01Mo-0.64Ni-0.39Cu (wt. %) weld deposit, isothermally transformed at 675 °C @ 50 s after austenitisation at 1000 °C @ 10 min. (b) TEM micrograph showing the inclusion assisted nucleation of acicular ferrite plates in Fe-0.06C-0.27Si-1.84Mn-2.48Ni-0.2Mo wt. % weld deposit, isothermally transformed at 460 °C @ 30 min after austenitisation at 1200 °C @ 30 min (after Yang, 1987).

Martensite is a product of diffusionless transformation and can occur in the form of thin, lenticular plates, which often extend right across  $\gamma$  grains, or as packets of approximately parallel, fine laths, whose size is generally less than that of the  $\gamma$  grains. In both cases the parent and product crystals are related by an atomic correspondence and the formation of martensite causes the shape of the transformed region to change, this shape change is macroscopically an invariant-plane strain, the invariant-plane being the habit plane of martensite. The nucleation of martensite is generally athermal (but can be isothermal) and is believed to be diffusionless in nature. Martensite can occur at very low temperatures and its interface with the parent phase necessarily has to be glissile. Martensite forms at high undercoolings where the chemical free energy change for transformation is generally very large, well in excess of that required to accomplish diffusionless transformation even when the stored energy of the martensite is taken into account. Fig. 1.17 shows the formation of martensite in Fe-0.12C-0.3Si-0.5Mn-1.0Mo-2.5Cr (wt. %) alloy steel.



Fig. 1.17: Micrographs showing martensite transformation in alloy of composition Fe-0.12C-0.3Si-0.5Mn-1.0Mo-2.5Cr (wt. %) steel quenched directly from 940 °C.

# 1.10 Summary

A literature survey on some of the basic concepts of phase transformations in steels has been presented. The decomposition of austenite below the  $Ae_3$  temperature can result in the formation of a varieties of reconstructive and displacive transformation products, which can be distinguished by the features such as shape deformation, thermodynamics, and morphology.

# \*\*\*

# Chapter 2 REAUSTENITISATION

The following chapter is a survey of the work in the published literature, on the formation of austenite, including an assessment of the kinetics of austenite formation.

# 2.1 General Introduction

The process of reaustenitisation is an important phenomenon and is of considerable industrial importance. It plays an important role in several methods involving the heat-treatment of steels. For example, the dual phase steels§ produced by intercritical annealing of low carbon alloy steels in the  $\alpha + \gamma$  phase field to generate a mixture of ferrite and austenite, which is then quenched to induce martensitic transformation of the austenite (Fig. 2.1). Austenite formation is also important in many fabrication processes involving multipass welding. Although the growth of austenite during heating of steels above the eutectoid temperature was studied by Hultgren [1929], Roberts *et al.* [1943], Baeyertz [1942] many decades ago there is as yet no adequate theory on the reverse transformation from ferrite in quantitative terms.

The ferrite-martensite dual phase steels, which provide a good combination of strength and ductility have been extremely successful in producing dramatic reductions in the weight of cars. It has been shown that at a given tensile strength level, dual phase steels have superior formability to standard high strength low alloy (HSLA) steels [Hayami and Furukawa, 1975; Rashid and Rao, 1981]. Such steels are now used widely in the automobile industry because of their high strength to weight ratio, a desirable target in the automobile industry for the sake of fuel efficiency and performance.

There are two different approaches in the production of dual phase steels [Hayami *et al.* 1979]. One of them involves a combination of the accelerated cooling of austenite followed by slower cooling at around the ferrite transformation-start temperature  $Ae_3$ . This method provides the as hot-rolled dual phase steels

<sup>§</sup> Dual phase steels consist of a strong phase 'martensite' as a load carrying constituent in a ductile ferrite matrix. The martensitic regions may be, in fact, contain some retained austenite and/ or lower bainite as well, depending on the chemical composition and the cooling rate of the steel [Rashid and Rao, 1981].



## Fig. 2.1: Schematic representation of heat treatments to produce dual phase steels.

which are cheaper than those produced after cold rolling followed by intercritical annealing at temperatures between  $Ae_1$  and  $Ae_3$ . In this latter heat treatment, a certain volume fraction of austenite, which has been produced by intercritical annealing, is surrounded by soft ferrite particles and the austenite then transformed into martensite during a final quenching process. In both processes, the amount, hardness and distribution of martensite, and the ferrite grain size determine the ultimate mechanical properties of the dual phase steel. The microstructure just before the final quench in the intercritical annealing method must therefore, be predicted precisely to achieve the optimum properties.

In multirun welds, the heat input associated with the deposition of successive layers of weld metal causes some or all of the underlying structure to be reheated to temperatures where austenite formation occurs [Yang and Bhadeshia, 1987a]. The new austenite then transforms again during cooling to a microstructure which is generally very different from the solidification structure associated with weld deposits, and can seriously effect the mechanical properties of the final weld.

# 2.2 Effect of Initial Microstructure

The kinetics of reaustenitisation and the nature of the transformation products depend strongly on alloy chemistry, the initial microstructure and heating rate. A lot of research dealing with the initial microstructure effect on the morphology of austenite, has already been done [Baeyertz, 1942; Judd and Paxton, 1968; Law and Edmonds, 1980; Lenel and Honeycombe, 1984; Yang and Bhadeshia, 1987b; 1989; 1990; Yang, 1988]. The morphology of austenite may be divided roughly into two types; "acicular" and "globular". Some workers have further characterised the austenite as grain boundary allotriomorphic, sawteeth, grain boundary idiomorphs and Widmanstätten, morphologies, similar to the terminology common to the decomposition of austenite [Lenel and Honeycombe, 1984a; Plichta and Aaronson, 1974]. There is much less information on the transformation from the initial microstructure which is fully ferritic, or which contains a mixture of just bainitic ferrite and austenite, compared with other initial microstructures such as pearlite, a mixture of pearlite and ferrite and a mixture of carbides and martensite.

# 2.2.1 Effect of Deformation on Austenite Formation

Austenite formation in cold rolled steels is complicated by the recrystallisation of cold worked ferrite. Cold rolling serves to disperse and deform the pearlite, and the rapid spheroidisation of pearlitic cementite has occurred early in the intercritical annealing cycle [Yang *et al.* 1985]. Austenite forms on and around the spheroidised carbide particles, and the initial growth of austenite is accomplished by dissolution of carbide particles through the austenite to the austenite-ferrite interfaces.

Yang *et al.* [1985] showed that in cold rolled steels, austenite formed not only at ferrite boundaries but also within the ferrite grains. They also showed that austenite formed first on the boundaries between deformed and unrecrystallised ferrite grains and then on spheroidised cementite particles in recrystallised ferrite grains as illustrated in Fig. 2.2.

# 2.2.2 Reaustenitisation from a Mixed Ferrite and Pearlite Microstructure

The formation of austenite from a pearlitic microstructure was studied at an early stage in research on reaustenitisation [Hultgren, 1929; Baeyertz, 1942]. This work has been reviewed for application to ferrite-martensite dual phase steels. The nucleation of austenite in eutectoid steels has been reported to occur preferentially at the intersection of pearlite colonies [Roberts and Mehl, 1943].



Fig. 2.2: Schematic illustration of the austenite ( $\gamma$ ) formation during low temperature intercritical annealing of a ferrite-pearlite microstructure [Speich et al. 1981]. a) Ferrite-pearlite starting structure. b) Spheroidisation of cementite and coarsening of cementite particles at  $\alpha - \alpha$  boundaries. c) Nucleation of  $\gamma$  at cementite particles on  $\alpha - \alpha$  boundaries. d) Nucleation of  $\gamma$  on cementite particles within the spheroidised pearlite colony and growth of austenite on  $\alpha - \alpha$  boundaries.

In spite of the large area per unit volume, the inter-lamellar surfaces do not seem to act as the nucleation sites for austenite [Speich and Szirmae, 1969], although a reasonable explanation for this is not yet available. In addition, the fact that the formation of austenite is found to occur at the interfaces between ferrite grains and pearlite colonies instead of at the inter-lamellar surfaces (in the case of the mixture of ferrite and pearlite starting microstructure), suggests the importance of ferrite-ferrite grain boundaries for the nucleation of austenite [Roberts and Mehl, 1943; Lenel and Honeycombe, 1984a; Speich and Szirmae, 1969; Cai *et al.* 1985 and Garcia and DeArdo, 1981]. Garcia *et al.* [1981] have studied the formation of austenite from a mixture of ferrite and pearlite and concluded that austenite appeared to nucleate on cementite particles which were located on either pearlite colony boundaries or boundaries separating pearlite colonies and ferrite grains. The same results have been reported by Speich *et al.* [1969] in the case of the formation of austenite in eutectoid steels.

### 2.2.3 Reaustenitisation from Ferrite and Spheroidised Cementite

The mixture of ferrite and spheroidised cementite can be obtained by tempering martensite at a certain temperature. After tempering, most cementite particles tend to locate at the ferrite/ferrite grain boundaries instead of within the ferrite grains while in materials which have been tempered after cold working, most of the cementite particles are dispersed in the ferrite matrix away from the ferrite grain boundaries [Speich and Szirmae, 1969]. Using this technique, the role of cementite particles and ferrite grain boundaries for the nucleation and growth of austenite from a mixture of spheroidised cementite has been studied by several researchers [Judd and Paxton, 1968; Lenel and Honeycombe, 1984; Speich and Szirmae, 1969; Garcia and DeArdo, 1981]. In steels having a low number density of nucleation sites i.e., those which have few carbides at grain boundaries relative to the total amount of carbide, the growth of austenite will be controlled largely by the dissolution of carbides in ferrite ahead of the interface and diffusion of carbon through ferrite to the advancing interface. This produces Widmanstätten side-plates or sawteeth morphologies of austenite [Lenel and Honeycombe, 1984a].

Yang et al. [1985; 1985b] have studied the formation of austenite from ferritespheroidised cementite microstructures. They showed that the spheroidisation of cementite particles plays an important role in the development and distribution of austenite during low temperature intercritical annealing. Austenite forms on and around the spheroidised carbide particles, and that the initial growth of austenite is accomplished by the dissolution of cementite particles and the diffusion of carbon from the particles through the austenite to austenite-ferrite interfaces. This process directly led them to the distribution of austenite at grain boundary allotriomorphs and intragranular idiomorphs in specimens intercritically annealed at low temperatures. Nehrenberg [1950] noticed that "acicular" austenite grains developed from spheroidised ferrite/cementite structures only if they were produced from martensite rather than pearlite. Dirnfeld *et al.* [1974] have studied the formation of austenite in a fine grained tool steel. They demonstrated that nucleation starts at carbides which lie at the ferrite grain boundaries.

# 2.2.4 Reaustenitisation from Martensitic Microstructures

Recently a number of investigators have examined in detail the formation of austenite from martensite in low carbon steels. Both acicular and globular austenite morphologies were observed [Kinoshita and Ueda, 1974; Matsuda and Okamura, 1974; Matsuda and Okamura, 1974; Homma, 1974, Watanabe and Kunitake, 1975]. It is generally agreed that accular austenite is inherited initially from the elongated nature of the prior martensite laths and/ or packets, and is favoured by slow heating rates [Kinoshita and Ueda, 1974; Matsuda and Okamura, 1974; Matsuda and Okamura, 1974], low austenitising temperatures and acicular starting microstructures, such as tempered martensite, where lath boundaries are well decorated by carbide precipitates [Homma, 1974; Watanabe and Kunitake, 1975]. It has also been demonstrated that each acicular austenite grain formed from ferrite laths with the same orientation has the same crystallographic orientation and has the Kurdjumov-Sachs (K-S) orientation relation with the ferrite [Watanabe and Kunitake, 1975]. In the later stages of the transformation, more acicular austenite grains were forced to nucleate within the ferrite regions and eventually the austenite grains coalesce to assume a globular morphology.

Reaustenitisation of martensite has been studied in ferrite-martensite dual phase steels which are obtained by intercritical annealing followed by quenching to ambient temperature to get the appropriate mixture of ferrite and martensite. Nucleation of austenite occurs preferentially at the prior austenite grain boundaries [Baeyertz, 194; Matsuda and Okamura, 1974; Homma, 1974; Law and Edmonds, 1980]. Acicular austenite forms within the prior austenite grains of the martensitic, bainitic structures, and the grains soon coalesce to form globular austenite grains Law and Edmonds, 1980; Watanabe and Kunitake, 1975; Watanabe and Kunitake, 1975]. Watanabe et al. [1975] studied reaustenitisation from martensite microstructure in two types of steels, Fe-0.13C-0.25Si-0.76Mn-0.19Cu-0.98Ni-0.5Cr-0.51Mo and Fe-0.40C-0.12Si-9.16Ni (wt. %). They found that austenite formed with an acicular shape with each acicular austenite grain having the same orientation, the Kurdjumov-Sachs relationship with the ferrite. Law et al. [1980] found that austenite allotriomorphs nucleated on ferrite grain boundary bear a K-S orientation relationship to one of the ferrite grains, and grow into the adjacent grain by the migration of an incoherent interface.

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Chapter 2

### 2.2.5 Reaustenitisation from Ferrite

Little work has been done on reaustenitisation of ferritic samples because of the extremely low hardenability of these steels, which makes it almost impossible to freeze the austenite microstructure to ambient temperature even in the form of martensite phase. Speich *et al.* [1969] studied the formation of austenite in low carbon steel using laser-pulse heating and a helium-water droplet spray technique which allows  $10^6 \ ^{o}$ C s<sup>-1</sup> of heating rate and  $10^5 \ ^{o}$ C s<sup>-1</sup> of cooling rate. They showed that the formation of austenite had occurred at the ferrite/ferrite grain boundaries where they found fine ferrite grains transformed from austenite which grew during the rapid heat treatment.

#### 2.2.6 Reaustenitisation from Bainitic Ferrite

A little work has been reported in the past dealing with the formation of austenite from bainitic microstructures including acicular ferrite. The formation of austenite from bainitic microstructures has been studied by Nehrenberg, [1950]; Matsuda *et al.* [1974a, 1974b]; Matsuda and Okamura, [1974], Law *et al.* [1980], Yang *et al.* [1987]; Yang, [1988]; Yang *et al.* [1989] Yang and Bhadeshia, [1990]. Law *et al.* [1980] have reported that the nucleation of austenite had occurred primarily at the prior austenite grain boundaries and that site saturation occurred after rapidly. Isothermal reaustenitisation at high temperatures seemed to lead more intragranular nucleation of austenite.

Recently, Yang and Bhadeshia, [1987, 1989] and Yang, [1988] have investigated the growth of austenite from bainite and acicular ferrite. They studied isothermal and continuous heating transformations from upper bainite and acicular ferrite in a matrix of austenite. The starting microstructures thus already contained austenite, whose nucleation is consequently unnecessary during heating. With isothermal transformation, they found that reverse transformation did not happen immediately the temperature was raised above that at which the bainite or acicular ferrite had formed, even though the alloy was within the intercritical region of the phase diagram. They modelled the growth of austenite in terms of one dimensional carbon diffusion-controlled movement of planar austenite/ferrite interfaces, as shown in Fig. 2.3.



Fig. 2.3: Schematic diagram showing the model for one dimensional carbon diffusion-controlled growth of austenite [after Yang, 1988].

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#### 2.3 Crystallography of Austenite

Watanabe *et al.* [1975] found that each austenite grain which has been formed from ferrite laths with the same orientation and the austenite has the K-S orientation relationship with the ferrite. Both lath boundaries and cementite play an important role in the formation of austenite grains, with same orientation. When austenite is formed adjacent to precipitated cementite on the boundary, the austenite must have Pitsch orientation relationship with cementite and K-S orientation relationship with ferrite. Lenel *et al.* [1984] have shown that the grain boundary nucleated austenite shows a Kurdjumov-Sachs orientation relationship with one or both ferrite grains on either side of the grain. The orientation relationship between acicular austenite and martensite matrix has been reported to represent the Kurdjumov-Sachs orientation relationship [Matsuda and Okamura, 1974].

### 2.4 Effect of Heating Rate on Reaustenitisation

The heat treatment conditions can also influence the morphology of austen-Acicular austenite seems to be inherited from the elongated nature of the ite. prior martensitic laths and/or packets and is formed by slow heating rates and low austenitisation temperatures. Globular austenite appears favoured by the opposite conditions to those described above [Law and Edmonds, 1980]. Kinoshita et al. [1974] studied the effect of heating rate in the range of 2  $^{\circ}$ C min<sup>-1</sup> to 2  $^{\circ}$ C s<sup>-1</sup> from ferrite-pearlite and martensite initial microstructures. They found that heating of ferrite-pearlite at either heating rate gives rise to the nucleation of austenite at ferrite-pearlite interfaces and pearlite colony boundaries. They also indicated that heating of martensite at 2  $^{\circ}$ C s<sup>-1</sup> produces a smaller amount of acicular austenite and a large amount of granular austenite at prior austenite grain boundaries. Slow heating of martensite at 2 °C min<sup>-1</sup> however, produced a large amount of acicular austenite in the prior austenite grain interior along with globular one at the boundaries, which comes to compose a lameller structure of austenite and acicular ferrite. Law and Edmonds, [1980] shows that as the heating rate was lowered the distribution of austenite nuclei become concentrated around the prior austenite grain boundaries in the martensite and bainitic structures and the ferrite grain boundaries in the ferrite structures. At very low heating rates, the growth of austenite tended to be allotriomorphic, even in the martensite and bainitic microstructures. Yang et al. [1990] studied the effect of heating rates on the reaustenitisation from martensitic microstructure in Fe-C-Si-Mn alloy. They found that the transformation start temperature is raised as the heating rate increased (Fig. 2.4).

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Fig. 2.4: Effect of heating rate on the austenite formation-start temperature during continuous heating in homogenised Fe-C-Si-Mn-Ni weld deposits [after Yang 1987].

### 2.5 Effect of Alloying Elements on the Morphology of Austenite

The strength and ductility shown by dual phase steels are dependent upon the relative proportions of martensite and fine grained ferrite; the alloy will be stronger but less ductile if a larger percentage of martensite is present in the structure. The percentage of martensite in the dual phase structure will be dependent upon; (a) the carbon content, (b) the annealing temperature, and (c) the hardenability of the austenite region.

Plichta *et al.* [1974] have studied the effect of alloying elements on the formation of austenite by classifying alloy systems into different groups according to the observed morphologies of austenite. They concluded that it is a competition between the nucleation and growth of austenite at lath boundaries and the migration of these boundaries which determine the shape of the final product. However, their explanations are inconclusive. For example, they have not recognised the effect of alloying element concentrations on the morphology of austenite thus formed. An 'acicular' austenite morphology was observed in a Fe-0.5Cr-0.1C (wt. %) dual phase steel, whereas a globular austenite morphology was obtained in a Fe-4Cr-0.1C (wt. %) dual phase steel. Lenel *et al.* [1984] studied the formation of austenite from a starting microstructure consisting of ferrite and  $M_{23}C_6$  carbides (coarse at grain boundaries and fine in the matrix). The nucleation of austenite is relatively sluggish, while the growth occurs rapidly (completed within 100 seconds at temperatures above  $Ae_3$ ). The austenite inherits the Cr content of ferrite and no partitioning of Cr between ferrite and austenite accompanies the transformation.

Addition of alloying elements also affects the rate of formation of austenite; for example Judd *et al.* [1968], studied the effect of manganese on the formation of austenite. They found that Mn increases the incubation time for the nucleation and lower the nucleation rate of austenite. Although they explained the effect of Mn in terms of the carbide stability and diffusion fluxes in the system, but this seems to be somewhat speculative because manganese is an austenite stabilizer and should favour the formation of austenite.

#### 2.6 An Assessment of the Kinetics of Reaustenitisation

#### **2.6.1** Nucleation of Austenite

The kinetics of reaustenitisation are known to be a nucleation and growth process [Roberts and Mehl, 1943]. The nucleation site, growth rate and austenite morphology depend strongly upon on the initial microstructure of steels. Yi et al. [1985] studied the austenitisation process in an Fe-0.04C-2.20Si-1.8Mn (wt. %), and concluded that austenite is preferentially formed along the ferrite grain boundaries. Austenite formation along the grain boundaries proceeds rapidly, but its growth slows down after the site-saturation with austenite particles has occurred. The preferential sites for the nucleation of austenite are ferrite/ferrite grain boundaries in the case of the ferrite single phase starting microstructures [Speich and Szirmae, 1969, junctions of carbide particles and ferrite grain boundaries in the case of mixture of ferrite and carbide starting microstructures Judd and Paxton, 1968; Lenel and Honeycombe, 1984a; Speich and Szirmae, 1969; Garcia and DeArdo, 1981] junctions between pearlite colonies and ferrite grain boundaries in the case of the mixture of pearlite and ferrite starting microstructures [Roberts and Mehl, 1943; Lenel and Honeycombe, 1984a; Speich and Demarest, 1981, Cai et al. 1985, Garcia and DeArdo, 1981 junctions between pearlite colonies in the case of pearlite

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starting microstructures [Robert and Mehl, 1943; Speich and Demarest, 1981] prior austenite grain boundaries or martensite lath boundaries in the case of martensite starting microstructures [Baeyertz, 1942; Law and Edmonds, 1980; Matsuda and Okamura, 1974; Matsuda and Okamura, 1974] and prior grain boundaries in the case of bainite starting microstructures. In addition to these nucleation sites, carbide particles located at the boundaries between pearlite colonies and ferrite grains [Garcia and DeArdo, 1981], ferrite/ferrite boundaries and the retained austenite trapped between martensite laths [Yang and Bhadeshia, 1987; Yang, 1988; Yang and Bhadeshia, 1989; 14] have also been pointed out to play an important role for the nucleation of austenite.

#### 2.6.2 The Growth of Austenite

The mechanism which governs the growth rate of austenite during reverse transformation from martensite, bainite and single phase ferrite has not been established. In the case of reaustenitisation from pearlite, the mixture of ferrite and pearlite, and the mixture of ferrite and spheroidised carbides, the growth of austenite is controlled by the diffusion of carbon in the austenite in the early stage of transformation [Speich and Demarest, 1981; Speich and Szirmae, 1969; Judd and Paxton, 1968; Lenel and Honeycombe, 1984a, 1984b; Hillert *et al.* 1971].

When the starting microstructure is pearlite, at high reaction temperatures, the partitioning of substitutional atoms becomes negligible because of the high supersaturation. In this case the diffusion of substitutional atoms is limited to an extremely short range although the long range diffusion of carbon atoms can occur with a diffusion distance about equal to the inter-lamellar spacing of the pearlite as discussed by Speich *et al.* [1981]. At low temperatures, in contrast, the long range diffusion of substitutional atoms might occur because of the low supersaturation, and the partitioning under local equilibrium at the interfaces will be achieved.

These two types of growth kinetics may appear at the first stage of the formation of austenite from the mixture of ferrite and pearlite until the dissolution of pearlite is complete.

After the completion of carbide dissolution in the mixture of ferrite and austenite, the situation might be same as that in the mixture of ferrite and carbides. In these cases, the kinetics governing the growth of austenite depend not only on the distribution of carbides [Hillert *et al.* 1971] or pearlite colonies but also on the reaction temperature. When carbides or pearlite colonies are distributed sparsely, interference between growing particles of austenite is negligible and the growth of austenite in this situation will be controlled by carbon diffusion in austenite. For closely spaced carbides carbon diffusion in both austenite and in adjacent ferrite controls the growth of the austenite. At sufficiently low temperatures substitutional elements also diffuse during austenite growth.

In the case of the starting microstructure of martensite or bainite, the mechanism of the growth of austenite may be influenced by the carbides which have been formed during heat treatment or which exist in the initial microstructure. In these microstructures, the excess carbon exists either as carbides at ferrite grain boundaries or within the ferrite grains, or as solute in retained austenite or in martensite. The excess carbon trapped in the retained austenite or martensite may be exhausted by carbide precipitation during a heat treatment. The kinetics will then be the same as discussed in the case of the formation of austenite from the mixture of ferrite and carbides.

According to recent investigations [Yang and Bhadeshia, 1988, 1989, 1990; Yang, 1987] on reaustenitisation from a mixture of bainitic ferrite and residual austenite, the growth of austenite can satisfactorily be modelled in terms of onedimensional carbon diffusion-controlled movement of the planar austenite-ferrite interfaces.

#### 2.7 Summary

A survey of currently available literature on the formation of austenite has been presented. It can be concluded that both the nucleation and growth of austenite are largely dependent upon the initial microstructure, heating rate, and alloying elements. The preferred nucleation sites for the austenite are ferrite/ferrite grain boundaries or junctions of carbide and ferrite grain boundaries or prior austenite grain boundaries. The morphology of austenite also depends on the initial microstructure. If initial microstructure consists of ferrite laths for example bainite or martensite, the austenite adopts an acicular morphology otherwise grow in a globular morphology.

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# Chapter 3 EXPERIMENTAL: PROCEDURES AND TECHNIQUES

This chapter contains a brief description of the experimental alloys, heat treatments and other experimental procedures used in the research. Since the ultimate aim to was to lay down the foundation for the modelling and prediction of the microstructures of high-strength steel weld deposits based on more rigourous theory, the microstructure as well as the behaviour under isothermal and continuous heating and cooling conditions, in order to establish the effects of parameters such as, alloy chemistry, cooling rate, *etc*.

# 3.1 Materials Selection

Since this study is mainly concerned with the Widmanstätten ferrite and bainite transformations, the selection of materials for this study was made, bearing in mind the following points:

- The materials should be of a high purity.
- The materials in some cases should have two separate C curves in the TTT diagram to avoid interference between Widmanstätten ferrite and bainite with the other transformations such as pearlite in the case of Widmanstätten ferrite and cementite precipitation in the case of bainite.
- The alloys should have at least two significantly different rates of transformation to cover all the morphologies of Widmanstätten ferrite and for the essence of the surface relief experiments.

It is already established that steels containing a large silicon concentration, bainite formation can occur without the precipitation of cementite [Bhadeshia and Edmonds, 1979, 1980, 1983]. Hence, high silicon alloys with different carbon concentrations were chosen. Because an aim of the present investigation is to improve the modelling of high strength steel weld deposits, some actual weld deposits were also studied. The chemical composition of all the alloys are given in Table 3.1. Alloys A1, A2, A3 and A4 ingots were hot rolled into round bars of 10 mm diameter. W1 was prepared by manual metal arc welding (MMA). The welding was carried out in the flat position using the stringer bead technique, the parent plate thickness being 20 mm. The welding current and voltage used were 180A and 23V (DC+) respectively (arc energy = 2 kJ mm<sup>-1</sup>), the weld consisting of some 21 runs with 3 runs per layer deposited at a speed about  $0.002 \text{ ms}^{-1}$ , the electrode diameter was 4 mm. These weld deposits were provided by ESAB (UK) Ltd.

Alloy	by design. Chemical Composition												
					$(\mathrm{wt}\%)$								)
	С	Si	Mn	$\mathbf{Cr}$	Mo	Ni	Cu	Nb	V	Ti	Al	0	Ν
A1	0.220	2.07	3.00	-	0.00	-	-	-	-	-	-	6	-
A2	0.220	2.05	3.07	-	0.70	-	-	-	-	0.004	0.005	94	-
A3	0.120	0.30	0.50	2.50	1.00	-	-	-	-	-	-	-	-
A4	0.400	2.00	-	-	-	-	-	-	-	-	-	-	-
A101	0.059	1.96	2.88	-	-	-	-	-	-	-	-	-	-
A102	0.120	2.03	2.96	-	-	-	-	-	-	0.004	0.005	14	-
A103	0.059	1.94	-	-	-	4.07	-	-	-	0.004	0.009	1900	-
A104	0.096	2.00	-	-	-	4.07	-	-	-	-	-	-	-
W-1	0.067	0.44	1.22	0.50	0.01	0.64	0.39	0.01	0.02	-	-	350	91

Table 3.1: Chemical composition of the materials used in present study.

## **3.2 Specimen Preparation**

Two types of specimens were used; 10 mm long rods of 3 mm diameter were used for isothermal heat treatments and optical microscopy. The 3 mm diameter was selected to facilitate transmission electron microscopy at any stage of the experiments. Whereas 10 mm square rods were used, for surface relief experiments.

The 3 mm diameter rods were produced by swagging, involving a successive reduction in the diameter in approximately 1 mm steps. It was necessary to initially hot swagged down to 6 mm diameter rod. After removing 2 mm from the surface, these were further swagged down to 3 mm rods at ambient temperature in order to avoid oxidation.

#### **3.3 Heat Treatment Procedures**

The heat treatment cycles are illustrated Fig. 3.1 and are described below:

#### 3.3.1 Homogenisation

After swagging, the 3 mm diameter rods were homogenized at 1250 °C for 3 days while sealed in quartz tubes containing a partial pressure of high purity

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argon. The homogenisation treatment was carried out in a resistance-heated horizontal tube furnace and the temperature was measured with a Pt-Pt 13 wt% Rh thermocouple. The temperature was controlled within the limits of  $\pm$  5 °C.

# **3.3.2** Austenitisation

Before any isothermal transformation austenitisation treatments generally performed at 1100 °C for 10 min to produce larger austenite grains, while the specimens were sealed in quartz capsules under a partial pressure of pure argon.

# 3.3.3 Isothermal Transformation

After austenitisation the samples were taken out from the furnace, the quartz capsule was carefully broken and then immediately quenched into a fluidized bed, which was maintained at the reaction temperature (controlled to  $\pm$  3 °C ), for specified duration and then finally quenched into iced-water.

It was felt essential to break the silica capsules before the commencement of isothermal transformation, to bring the specimen concerned to the transformation temperature as quickly as possible.

The powder in the bed was fluidized by introducing air through the bottom of the bed. The flow rate of the air in the outer chamber was maintained at 250 cm<sup>3</sup> min<sup>-1</sup>, while in the inner chamber it was 84 cm<sup>3</sup> min<sup>-1</sup>. A uniform temperature was maintained in the fluidized bed under these flow conditions.

#### **3.4 Surface Relief Experiments**

For surface relief experiments, specimens were mechanically polished to a 1/4  $\mu$ m finish, and sealed in quartz capsules. Before sealing, the capsules were flushed several times with high purity argon gas to minimize oxidation at the mirror-surface of the specimen. The capsules were finally sealed off with a partial pressure of argon. The heat treatments were carried out in the same way as described in the previous section except that after austenitisation, the quartz capsules were not broken but simply transferred to the fluidized bed maintained at the reaction temperature, reacted for the predetermined time and then quenched into ice cooled water.

Any surface relief effects were imaged using the Nomarski differential interference technique with a Ziess optical microscope. The tilt sense was determined by through focusing experiments, using grain boundary grooves for reference. Upward upheavals consisting of two adjacent and opposing invariant-plane strains are referred to as "tent-like" compared with a similar net depression of the free surface which are referred to as "vee-shaped" surface relief effects.

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Fig. 3.1: Continued.....











Fig. 3.2: Photograph showing the dilatometer and its test chamber, as used in this study.

#### 3.5 Dilatometry

Dilatometry is a powerful technique to study the kinetics of phase transformation. All dilatometry was performed on a Theta Industries high speed dilatometer (shown in Fig. 3.2), which has a water cooled radio-frequency furnace of essentially zero thermal mass, since it is only the specimen which undergoes the programmed thermal cycle. The length transducer on the dilatometer was calibrated using a pure platinum specimen of known thermal expansion characteristics. The dilatometer has been specially interfaced with a BBC/Acorn microcomputer so that length, time and temperature information can be recorded at microsecond intervals during the heat cycle, and the data are stored on a floppy disc. The information is then transferred to a mainframe IBM3084 computer for further analysis.

# **3.5.1** Specimens for Dilatometry

Two types of specimen were used, solid cylindrical (SC) and hollow thin walled cylindrical (HTWC) as shown in Fig. 3.3, depending upon the transformation kinetics of the material. SC specimens for dilatometry were machined in the form of 3 mm diameter rods with about 20 mm of length. To obtain higher heating or cooling rates HTWC specimens were machined in the form of 4 mm diameter rods



Fig. 3.3: Schematic diagram of the specimens used; a) for dilatometry and b) for lattice parameter measurements.

with 2.5 mm bore through it, to get a reduced wall thickness with about 10 mm of length.

#### 3.5.2 Nickel Plating

To avoid surface nucleation and surface degradation, all dilatometry specimens were plated with nickel. This nickel plating process is in two stages; nickel striking and nickel plating. Striking was carried out in a solution made up of 250 g nickel sulphate, 27 ml concentrated sulphuric acid and distiled water, amounting to one litre in all, at 50 °C with a current density of 7.75 mA/mm<sup>2</sup> for three minutes. The plating solution consisted of 140 g nickel sulphate, 140 g anhydrous sodium sulphate, 15 g ammonium chloride and 20 g boric acid, was made up to one litre with distiled water. The plating was carried out at 50 °C with a current density of 0.4 mA/mm<sup>2</sup> for fifteen minutes. This two process finally give a plate thickness of approximately 0.08 mm.

#### 3.6 Metallography

For optical metallography the heat treated specimens were hot mounted in an acrylic plastic, and ground on silicon carbide paper in continuous flow of water. Care was taken during initial grinding to remove sufficient material to avoid any unrepresentative surface caused by decarburization during heat treatment. They were then mechanically ground to 1200 grade emery paper and finally polished with 6, 1, and  $1/4 \ \mu m$  diamond pastes respectively.

After final polishing, the specimens were thoroughly cleaned and washed in methanol. Optical specimens were etched in 2 Nital solution (2 ml of  $HNO_3$  in 100 ml of methyl alcohol) and were examined using an OLYMPUS microscope, fitted with a 35 mm camera.

#### 3.7 Transmission Electron Microscopy

Thin foil specimens were prepared for transmission electron microscopy from 0.25 mm thick discs slit from heat treated specimens used in the dilatometry. The discs were thinned to about 0.04 mm by abrasion on 1200 grade emery paper and then electro-polished in a twin jet electro-polisher using a 5% perchloric acid, 25% glycerol and 70% ethanol mixture solution at ambient temperature, at about 50 V. The microscopy was conducted on a PHILIPS EM400 transmission electron microscope operated at 120 kV.

The extraction replica technique is very useful for the study of carbide or precipitate phases in a metallic system. The main advantages of replicas over foils are that they eliminate any effects due to the steel matrix and thus enable the chemical composition of the carbides to be measured more accurately, and working with a magnetic specimen in the electron microscope is avoided. The replica is also very thin  $\simeq 100$ Å, has no self-structure and will not burn in an electron beam.

Carbon extraction replicas were prepared using the method described by Smith and Nutting [1956]. Firstly, the metal surface was prepared using the same method and etchant as for optical microscopy, and then a bluish-brown layer of amorphous carbon was deposited onto the metal surface using a vacuum evaporator. The film was then scored using a sharp blade to enable removal of several small sections covering the whole area of the sample, and then electrolytically etched in a solution of 5% chloral (hydrochloric acid in methanol) at +1.5V until the edges of the film began to lift away from the surface. The specimen was washed in ethanol, and then in distiled water in which the replicas floated off and were collected on copper grids. The replicas were then examined in the TEM usually using an accelerating voltage of 120kV.

#### 3.9 Microanalysis

All microanalysis carried out on EM 400T transmission electron microscope fitted with a LINK 860 energy dispersive analysis system. Standard thin foil correction programmes were used to compensate for X-ray detection efficiency and absorption. For quantitative analysis the specimen was tilted by 35° towards the detector in order to optimise the signal.

# 3.10 Measurement of Lattice Parameter

The detailed analysis of dilatometric data requires a knowledge of ferrite lattice parameter, since the addition of various alloying elements to pure iron not only effects their mechanical properties but also the lattice parameter of the crystals.

#### 3.10.1 Materials and Specimen Preparation

The lattice parameters of five different steels were measured, and the steels can be categorized into two groups i.e., Fe-C-Si-Mn steels and Fe-C-Si-Ni steels (Table 3.1)

Two types of specimens  $0.5 \pm 0.01$  mm wire and fillings were used (Fig. 3.3). Before preparation from bulk material, samples were annealed at 600 °C for 2 hr, while sealed in silica capsules under a partial pressure of argon, in order to induce the thermal decomposition of any retained austenite.

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The specimens were then machined from the annealed 3.0 mm diameter rods. After machining, specimens were chemically polished in a solution containing 5 % HF, 45 % H<sub>2</sub> O<sub>2</sub> and 50 % H<sub>2</sub> O in order to remove the surface by about 0.1 mm to relieve any stresses induced during the machining operation.

Filings were obtained from annealed specimens, and were then re-annealed in silica capsules containing pure argon atmosphere, at 600  $^{o}$ C for 1 hr and finally cooled in the furnace to room temperature.

Lattice parameter measurements were carried out using a Debye-Scherrer camera. In order to get sufficient number of reflections, zirconium filtered molybdenum  $K\alpha$  radiation was used.

#### 3.11 Hardness Testing

Macro hardness were measured with Vicker's hardness testing machine using 10 kg load. While micro hardness measurements have been carried out on a Leitz hardness measuring machine. This instrument equipped with a digital eyepiece to which a computer-counter-printer was attached. Specimens were polished and etched by 2% Nital before the measurement of micro hardness. The indentation load applied was either 0.0981 N or 98.1 N.

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# Chapter 4 STUDY OF THE BAINITE TRANSFORMATION USING DILATOMETRY

# 4.1 General Introduction and Scope

Classical bainite is a non-lameller mixture of ferrite and carbide [Davenport et al. 1930; Mehl, 1939], generally regarded as an aggregate of ferrite and residual phases, such as retained austenite, carbide or martensite. The bainite transformation is of particular importance to industry, because steels in the bainitic condition can show a very good combination of strength and toughness [Nakasugi et al. 1983]. It exhibits various features which are different from reconstructive§ transformations such as allotriomorphic ferrite and idiomorphic ferrite or even those which also form by a displacive§ transformation mechanism e.g., Widmanstätten ferrite, in which only the interstitials diffuse. Bainite nucleates with an equilibrium carbon content but grows without diffusion [Bhadeshia, 1981a]. It consequently stops growing when the carbon concentration of austenite reaches a value given by the  $T_0$  curve of the parent alloy. While Widmanstätten ferrite nucleates by the same mechanism, it grows by an equilibrium or paraequilibrium mechanism and does not show an incomplete reaction phenomenon§.

Dilatometry is an important tool for the study of phase transformations in steels and widely used in industry because of its sensitivity and accuracy. This technique, has in the past been applied to the study of the bainite transformations, but during without sufficient interpretation of the data, it has often been incorrectly assumed that the transformation can proceed to a point where all the austenite is consumed. This interpretation of experimental data has apparently misled several researchers [Ohmori *et al.* 1971; Umemoto *et al.* 1982].

as "incomplete reaction phenomenon".

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<sup>§</sup> Reconstructive transformations are those which form as result of lattice reconstruction process by diffusion [Bhadeshia, 1987].

<sup>§</sup> Displacive transformations are those which form without the reconstruction of lattice, atoms just displace in a manner that they can maintain correspondence between product and parent phase, these products show various features which are similar to martensitic transformation [Bhadeshia, 1987].

 $<sup>\</sup>S$  At any temperature (below  $B_S$ ), and in the absence of any interfering secondary reactions, only a limited quantity of bainite forms before the reaction terminates, which is far less than that expected by the Lever rule at that temperature. This premature termination of the bainite transformation is known

This work is aimed at the further exploration of aspects of bainite transformation in high-strength steels in the context of recent studies [Bhadeshia, 1982]. Steels containing about 2 wt.% silicon as an alloying element were used; these steels can be isothermally transformed to just bainitic-ferrite and residual austenite [Bhadeshia *et al.* 1979, 1983], the formation of carbides being completely suppressed. Hence, the kinetic measurements relate directly to the displacive formation of bainitic-ferrite, without interference from any of the additional, diffusional reactions (such as precipitation of carbides) which accompany the formation of bainite in conventional steels.

#### 4.2 Experimental Techniques

For the present study, those materials were selected in which bainite transformation can be studied without the interference of other transformations such as pearlite and precipitation of carbides. The chemical composition of the steels used are listed in Chapter 3, but are reiterated here for convenience (Table 4.1). The other details (such as microscopy) have been discussed fully in Chapter 3.

Steel	Chemical Composition (wt. %)								
	C	Si	Mn	Ni	Mo	Ti	Al	O (ppm)	
A2	0.22	2.05	3.07	-	0.7	0.004	0.005	94	
A101	0.059	1.96	2.88	-	-	-	-	-	
A102	0.12	2.03	2.96	-	-	0.004	0.005	14	
A103	0.096	2.0	-	4.07	-	0.004	0.009	1900	
A104	0.05	1.94	-	4.04	-	-	-	-	

Table 4.1: Chemical composition of the steels used in the present study.

#### 4.2.1 Lattice Parameter of Ferrite

To study phase transformations in steels using dilatometry, it is essential to have a knowledge of the lattice parameter of ferrite, since the addition of various alloying elements to pure iron not only effects their mechanical properties but also the lattice parameter of the crystals. Work was undertaken to measure the lattice parameter of ferrite for five of the steels used in the present studies.

Lattice parameter measurements were carried out using a Debye-Scherrer camera. In order to get a sufficient number of reflections, zirconium filtered molybdenum  $K\alpha$  radiation was used.

# 4.3 Results and Discussion

Using the films obtained using the Debye-Scherrer analysis, the distances between the  $\theta$  values (Bragg angles) were measured with a travelling microscope, and a pairs of vernier callipers. Each film was measured at least three times and mean values were taken for subsequent calculations as shown in Table 4.2.

From these data, the *d* spacings of the planes were obtained via the Bragg law and analysed by plotting  $dsin^2\theta$  or the Nelson-Riley function; both of these functions are based on the fact that errors are minimised at large values of  $\theta$  [Cullity, 1978]. This is because the angular position of the diffracted beam is much more sensitive to a given change in plane spacing when  $\theta$  is large than when it is small. Nelson and Riley [1945] and Taylor and Sinclair [1945] analysed the various sources of error, particularly absorption, which can be significant for steel specimens of the two functions, the relation suggested by Nelson and Riley holds quite accurately down to low values of  $\theta$ , so that calculate lattice parameter values were extrapolated against  $(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$  rather than  $\sin^2\theta$ . The results are shown in Fig. 4.1, and the measured values of lattice parameter (a) are given in Table 4.2.



(a)

(b)

Fig. 4.1: Continued.....

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Fig. 4.1: Extrapolation of measured d-spacings against Nelson-Riley function [1947], for alloys (a) A2, (b) A101, (c) A102, (d) A103, and (e) A104.

Steel	Measured Lattice Parameter (Å)
A2	$2.8670 \pm 0.001$
A101	$2.8739 \pm 0.003$
A102	$2.8730 \pm 0.002$
A103	$2.8722 \pm 0.001$
A104	$2.8702 \pm 0.001$

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Table 4.2: Measured lattice parameters of the steels used.

# 4.4 Expansivities of Ferrite and Austenite

The interpretation of dilatometer data also requires a knowledge of the expansion coefficients of ferrite  $(e_{\alpha})$  and austenite  $(e_{\gamma})$ . The ferrite expansion coefficient was determined by first tempering a specimen at 600 °C for 10 min to decompose any retained austenite and then recording the length change during heating and cooling at rate of 0.001 °C s<sup>-1</sup>. The measurements do not therefore account for the presence of a small amount of carbide phase. The graphs of relative length versus temperature are plotted in Fig. 4.2. The expansion coefficient of austenite was measured while the specimen was in the  $\gamma$  single-phase field (Table 4.3).

Table 4.3: Measured expansion coefficient of ferrite and austenite.

Steel	Expansion Coefficient ( $^{o}C^{-1}$ )						
	Ferrite	Austenite					
A2	$1.443 \times 10^{-5} \pm 0.004$	$2.205 \times 10^{-5} \pm 0.027$					
A101	$1.416 \times 10^{-5} \pm 0.044$	$2.010  imes 10^{-5} \pm 0.064$					
A102	$1.435 \times 10^{-5} \pm 0.002$	$2.0756 \times 10^{-5} \pm 0.010$					
A104	$1.401 \times 10^{-5} \pm 0.021$	$2.021 \times 10^{-5} \pm 0.020$					

# 4.5 Theory for the Conversion of Dilatometry Data

For the transformation of austenite ( $\gamma$ ) into a mixture of bainitic ferrite and carbon-enriched austenite, Bhadeshia [1982] has shown that the relative length change  $\frac{\Delta L}{L}$ , which is the observed length change divided by the length of the specimen, can be related to the volume fraction of ferrite ( $V_{\alpha}$ ) by the equation:



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Fig. 4.2: Showing the graph of relative length change versus temperature, from which the linear expansion coefficient of ferrite was obtained in alloy (a) A2, (b) A101, (c) A102, (d) A104.

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$$\frac{\Delta L}{L} = \frac{2V_{\alpha}(\mathbf{a}_{\alpha}^{3}) + (1 - V_{\alpha})(\mathbf{a}_{\gamma}^{3}) - \mathbf{a}_{\gamma_{o}}^{3}}{3\mathbf{a}_{\gamma_{o}}^{3}}$$
(4.1)

with

$$\begin{split} \mathbf{a}_{\alpha} &= \mathbf{a}_{\alpha_{o}}(1 + e_{\alpha}(T - 25)) \\ \mathbf{a}_{\gamma_{o}} &= (C_{1} + C_{2}\overline{x} + C_{Si}x_{Si} + C_{Mn}x_{Mn} + C_{Mo}x_{Mo})(1 + e_{\gamma}(T - 25)) \\ \mathbf{a}_{\gamma} &= (C_{1} + C_{2}\overline{x} + C_{Si}x_{Si} + C_{Mn}x_{Mn}C_{Mo}x_{Mo})(1 + e_{\gamma}(T - 25)) \end{split}$$

The Coefficients  $C_i$  have been determined by Dyson *et al.* [1970];  $x_i$  represent the concentrations of alloying additions.

The carbon content of residual austenite  $x_{\gamma}$  is related to the volume fraction  $V_{\alpha}$  of ferrite is expressed by

$$x_{\gamma} = \frac{\overline{x} - V_{\alpha}S}{1 - V_{\alpha}} \tag{4.2}$$

where  $\overline{x}$  and S are the average carbon concentration of the steel and carbon content of ferrite respectively. Equation (4.1) can be solved iteratively to give  $x_{\gamma}$  from  $\frac{\Delta L}{L}$ measurements.

#### 4.6 Bainite Transformation

Fig. 4.3 shows the bainitic microstructure in a Fe-C-Si-Mn alloy consisting of classical sheaves of bainite nucleating at prior austenite boundaries. Transmission electron microscopy revealed (as expected) that the sheaves were composed of much smaller sub-units of ferrite and the microstructure did not contain any carbide precipitation. Only bainitic ferrite and carbon-enriched austenite could be seen; the bainite reaction did not go to completion despite prolong periods of holding at isothermal transformation.

It was found that near the  $B_S$  temperature only very limited amount of austenite transformed to bainite but as the isothermal transformation temperature decreased, correspondingly larger quantities of bainite were observed (Fig. 4.4). It is clear that in the specimen transformed above the calculated  $B_S$  temperature (Table 4.4) *i.e.*, at 520 °C, there is very little bainite, while in the specimens transformed at 500 °C and 480 °C, a large degree of transformation can be observed.

The dilatometry results (Figs. 4.5 and 4.6) also showed the relative length change during the formation of bainite increases as the isothermal transformation temperature decreases below the  $B_S$  temperature. The amount of bainite formed is dependent on the transformation temperature below  $B_S$ , consisted with the optical microscopy.



(b)

(a)

Fig. 4.3: Micrographs showing bainite microstructure in alloy A2. (a) Optical micrograph. (b) TEM micrograph. Specimen isothermally transformed at 400 °C for 1000 s after austenitisation at 900 °C for 5 min.



(c)

(a)

(b)

Fig. 4.4: Optical micrographs showing the effect of isothermal transformation temperature on bainite formation in alloy A102. Specimens austenitised at 1300 °C for 10 min and isothermally transformed for 200 s at (a) 560 °C (b) 520 °C (c) 480 °C. Note that the amount of bainite increases as the isothermal transformation temperature decreases.



Fig. 4.5: Effect of isothermal temperature on the maximum relative length change observed by dilatometry in alloy A2.



Fig. 4.6: Effect of isothermal temperature on the formation of bainite below  $B_S$  temperature in alloy A2. Note that the maximum extent of bainite transformation is increases with an decrease in isothermal transformation temperature.



Fig. 4.7: Effect of isothermal temperature on the maximum relative length change observed by dilatometry in alloy A102.



Fig. 4.8: Effect of isothermal temperature on the formation of bainite below the  $B_S$  temperature in alloy A102. Note that the maximum extent of bainite transformation increases with a decrease in isothermal transformation temperature.

The reaction proceeds initially rapidly but after a period the decomposition slows down as is shown in Figs. 4.7 and 4.8.

Table 4.4: Calculated transformation-start temperatures for the steels studied (calculated by using the methods discussed by Bhadeshia and Edmonds, 1979; Bhadeshia, 1981c; 1981d.)

Alloy No.	$Ae_3$	$Ae'_3$	$W_S$	$B_S$	$M_S$
A2	812	773	700	477	338
A101	864	828	760	545	422
A102	812	776	745	520	390
A103	800	774	680	552	444
A104	812	784	680	564	460

In alloys A101 and A104, the bainite occurred very rapidly with some transformation happening during cooling to the transformation temperatures. It follows that the relative length change measured at the intended temperature  $T_i$ , should be corrected as follows [Yang and Bhadeshia, 1987] as shown in Fig. 4.9. In the absence of transformation during cooling to the isothermal transformation temperature, the length of the specimen will vary linearly with temperature as the sample contracts. Any deviation from linearity indicates transformation during cooling. If the lower temperature part of the curve is extrapolated to the reaction temperature, the vertical difference between the extrapolated line and the actual length change curve gives the true length change due to transformation, as if no reaction had occurred during cooling. The maximum corrected relative length change is then  $\Delta L_f$ instead of  $L_i$  as illustrated in the Fig. 4.9. It is necessary to remove the effect of the transformation during cooling to  $T_i$ , the length increment associated with cooling from  $T_s$  to  $T_i$ ;

$$\Delta L_f = L_i \{ 1 + e_\alpha (T_s - T_i) \} \tag{4.3}$$

The corrected relative length change for the data shown in Table 4.5 and are plotted in Fig. 4.10.

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Fig. 4.9: Schematic representation of the method used to correct the dilatometry data to take into account of the transformation during cooling before reaching to the isothermal transformation  $T_{\gamma}$ . Note that this type of correction is valid only if no other reaction interfere the bainite transformation.



Fig. 4.10a: Temperature versus relative length change curves for the alloy A101, illustrating the transformation during cooling to the isothermal transformation temperature.

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Fig. 4.10b: Temperature versus relative length change curves for the alloy A104, illustrating the transformation during cooling to the isothermal transformation temperature.

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Temperature <sup>0</sup> C	Alloy No.	Original data ( $\Delta$ L/L)	Corrected data ( $\Delta$ L/L)
500	A101	0.00230	0.0029
520	A101	0.00235	0.0037
540	A101	0.00215	0.0034
500	A104	0.002	0.0024
530	A104	0.0023	0.0027
560	A104	0.00275	0.00374

Table 4.5: Original data and corrected data for alloys the A101, A103, and A104.

### 4.7 Incomplete Reaction Phenomenon of Bainite

An interesting feature of bainite transformation is the existence of the "incomplete reaction phenomenon". At any temperature within the bainite transformation range, and in the absence of any interfering secondary reactions, such as carbides or pearlite, only a limited quantity of bainitic-ferrite forms before the reaction terminates. This premature termination occurs before the carbon content of the remaining austenite reaches the equilibrium level indicated by the extrapolated  $Ae'_{3}$  curve. The maximum extent of transformation that can be achieved increases with undercooling below the bainite-start  $(B_{S})$  temperature.

It is apparent from Figs. 4.7 and 4.9, that in none of the present experiments did the volume fraction of bainitic ferrite exceed 0.4, the experiments can be interpreted [Bhadeshia *et al.* 1980] to be in agreement with the growth of bainite occurring by the propagation of martensitic sub-units, since the degree of transformation obtained complies approximately with  $T_0$  or  $T'_0$  curves.

The thermodynamic methods and data necessary for the calculation of  $Ae'_{3}$ ,  $T_{0}$  and  $T'_{0}$  curves have been described elsewhere [Aaronson *et al.* 1966; Shiflet *et al.* 1978; Bhadeshia and Edmonds, 1980] and the stored energy was taken to be 400 J mol<sup>-1</sup>, according to Bhadeshia [1981]. The results are shown in Figs. 4.11 and 4.12. The experimental points refer to the carbon content of the residual austenite, following the rapid termination of the bainite reaction. They are calculated from the measured length changes by using Eq. 4.2. The Figs. 4.11 and 4.12 clearly indicate that the bainite reaction terminated before the carbon content of the residual austenite reaches the  $T'_{0}$ , represents the maximum tolerable carbon use for the formation of fully supersaturated bainitic



Fig. 4.11: Calculated phase diagram with experimental data of carbon content of austenite at the termination of isothermal bainite formation. (a) For alloy A2 and (b) For alloy A102. Note that the reactions stop well before  $Ae'_3$  curve.

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Fig. 4.12: Calculated phase diagram with experimental data of carbon content of austenite at the termination of isothermal bainite formation. (a) For alloy A101 and (b) For alloy A104. Note that the reactions stop well before  $Ae'_3$  curve.

ferrite if the stored energy of bainitic ferrite taken into account. It is clear from the microstructures shown in Figs 4.6-4.9, that the extent of transformation is a sensitive function of temperature and this is totally characteristic of the incomplete reaction phenomenon [Hehemann, 1970]. This result together with the carbon content of austenite at the termination of bainite reaction are considered to be particularly relevant since there is no interference from carbide precipitation during the upper bainitic ferrite reaction in these alloys. Any precipitation of carbide would naturally reduce the carbon content of the enriched austenite, thereby promoting further transformation. Hence in it can be concluded that the formation of bainite in the alloy studied follows an incomplete reaction phenomenon and confirms the results earlier investigations [Hehemann, 1970; Bhadeshia and Edmonds, 1979; 1980; Yang, 1987].

#### 4.8 Surface Relief

Examination of a pre-polished, austenite and isothermally transformed specimens revealed that surface displacements could be associated with the upper bainite (Fig. 4.13). The uniformity of interference contrast on the tilted surfaces illustrated in Fig. 4.13, indicates that the invariant plane strain nature of the surface relief. Such displacements are characteristic of martensitic transformations and are taken to imply that the sub-units propagate in a displacive manner. This observation of an IPS shape change due to the formation of bainite has been noted by several other researchers [Ko, 1953; Cottrell and Ko, 1953; Bhadeshia and Edmonds, 1980]. This results is fully consistent with the sub-unit morphology and their martensitic growth.



Fig. 4.13: Micrographs showing the surface relief exhibited by bainite formation in alloy A2. Specimen isothermally transformed at 400 °C for 1000 s after austenitisation at 900 °C for 5 min.

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### 4.9 Conclusions

The austenite to bainite transformation has been studied in Fe-C-Si-Mn and Fe-C-Si-Ni steels used dilatometry backed by optical and transmission electron microscopy. It is concluded that:

- Bainite forms with a sheaf morphology and each sheaf consisting of ferrite sub-units.
- The sheaves nucleate at prior austenite grain boundaries and grow inwards of the grain.
- The maximum extent of bainite formation is dependent on transformation temperature below the  $B_S$  temperature.
- The reaction terminates prematurely well before the austenite carbon content reaches the  $Ae'_3$  curve.
- The bainite formation terminate when the carbon content of residual austenite reaches at  $T'_0$ .
- The bainite reaction follow an incomplete reaction phenomenon.
- Formation of bainite exhibit an IPS surface relief.

All these conclusions are consistent with the diffusionless displacive formation of bainite and the sub-unit morphology of bainite.



# Chapter 5 TEMPERING OF BAINITE IN Fe-C-Si-Mn-Mo STEEL

Classically *tempering* is a process of reheating which is commonly applied in industry to martensitic steels in order to achieve required hardness and toughness properties. Tempering of bainitic microstructures is an important phenomenon from an industrial point of view both for wrought steels and for weld deposits. Many steel assemblies in power generation plant operate at 565 °C and these service conditions cause the tempering of the initial microstructure, which usually consists of a mixture of allotriomorphic ferrite and bainite [Bhadeshia, 1988]. It has been demonstrated by Irvine and Pickering [1960] that bainitic steels also show an improved combination of mechanical properties after tempering. In multilayered weld deposits, tempering and reaustenitisation are inevitable because the deposition of every new layer reheats those deposited previously. Weld microstructures often contains substantial quantities of intragranularly nucleated bainite, the so-called acicular ferrite. Therefore, the tempering process is equally important to weld deposits.

All these examples emphasise the importance of the tempering process and although a large amount of data are available on the tempering of quenched steels [Baker and Nutting, 1959; Irani and Honeycombe, 1955; Ohmori, 1972; Speich and Leslie, 1972], relatively little attention has been given to the tempering of bainite. The following chapter deals with a detailed microstructural analysis of tempering of bainite in an ultra high strength steel containing a strong carbide forming element Mo. This study implements some earlier work on a Fe-C-Si-Mn alloy by including the effect of alloy carbide formation. Particular attention is also given to see the effect of tempering on bainite morphology.

### 5.1 Experimental Procedures

The chemical composition of the steel selected for the present study has been given in Table 3.1 and designated as alloy A2. The steel was received in the form of 10 mm diameter bar, from which 3 mm diameter rods were prepared by swagging treatments§. All specimens were homogenised at 1200 °C for three days in vacuua and Ni-plated to avoid surface degradation during the subsequent heat treatments. A Theta Industries high speed dilatometer was employed for short time (< 16 hours) tempering, while for longer time tempering, electrical resistance heating furnaces

<sup>§</sup> The details of specimen preparation and experimental techniques have been described in Chapter 3.

were used. Fig. 5.1 shows schematically the heat treatment cycles used throughout the present study.



Fig. 5.1: Schematic representation of the heat treatment cycles used for the tempering of bainite.

The specimens were transformed to bainite at 400  $^{\circ}$ C and then rapidly heated to a higher tempering temperature *i.e.*, 620  $^{\circ}$ C, instead of quenching to ambient temperature. This avoids the formation of any martensite during cooling to ambient temperature.

The selection of the tempering temperature was critical because the purpose of tempering was to decompose the austenite. The tempering temperature must therefore be below the reaustenitisation temperature, which was determined to be about 660 °C using dilatometry (see Chapter 11 for details).

Thin foils were obtained from the heat treated samples by the methods described in Chapter 3. In order to follow up the precipitation sequence carbon

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extraction replicas were prepared using the method of Smith and Nutting [1957] as described in Chapter 3. Both thin foils and carbon extraction replicas were examined in a PHILIPS 400T transmission electron microscope operating at 120 kV and attached with an energy dispersive x-ray spectrometer to facilitate EDX analysis. Specimens for optical microscopy were prepared by conventional metallography techniques. The hardness was measured on a Vicker's hardness machine.

### 5.2 Results and Discussion

The microstructure observed after isothermal transformation to bainite is shown in Fig. 5.2.



Fig. 5.2: TEM micrographs showing bainite microstructure, specimen austenitised at 900 °C for 5 min and isothermally transformed at 400 °C for 1000 s.

### 5.2.1 TEM Study of Tempered Bainite

Optical microscopy (Fig. 5.3) did not reveal any clear changes in microstructure during the early stages of tempering, although a comparison of the samples tempered for 2000 s and 5 days shows changes in contrast. Attention was therefore focused on transmission electron microscopy, the as-transformed (untempered) microstructure being illustrated in Fig. 5.4.



(a) Tempered for 2000 s.



(b) Tempered for 4000 s.

Fig. 5.3: Continued.....



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(c) Tempered for 8000 s.



(d) Tempered for 16 hr.

Fig. 5.3: Continued.....



(e) Tempered for 2 days.



(f) Tempered for 5 days.

Fig. 5.3: Optical micrographs showing the effect of tempering time on the microstructure. All specimens were austenitised at 900 °C for 5 min, transformed to bainite microstructure at 400 °C for 1000 s and tempered at 620 °C.



Fig. 5.4: TEM thin foil micrograph showing bainite sheaves microstructure. Note the lenticular-plate morphology of bainitic ferrite sub-units, particularly the curved tip due to the constraint imposed by the matrix.

### 5.2.2 Precipitation of Carbides During the Tempering of Bainite

The formation of bainitic ferrite leads to an increase in the carbon concentration of the austenite which remains untransformed. The austenite eventually began to decompose to a mixture of carbides and ferrite. The precipitation process started first at the prior austenite/bainitic ferrite boundaries, as shown in Fig. 5.5. These precipitates identified as cementite by electron diffraction (Figs. 5.5, 5.6).

Microanalysis results on extracted carbides also demonstrate that their compositions were consistent with cementite (Table 5.2). More profuse precipitation followed prolonged tempering, but during these relatively early stages of tempering the carbide phase was identified to be rod-like cementite (Fig. 5.5). Fig. 5.6 shows that many of the carbides precipitated from the austenite films trapped between the bainitic ferrite sub-units, so that the decomposition of the austenite did not lead to any change in the bainitic ferrite plate shape, presumably because the carbides pin the sub-unit boundaries. The strong alignment of the carbides along the sub-unit boundaries is obvious in Fig. 5.6b, where the directions along which the carbides precipitate most preferably are seem to vary with the sheaf (and hence austenite films) orientation. Although the majority of carbides were identified clearly to be cementite (Fig. 5.7b, c), classical needle like Mo<sub>2</sub>C precipitates were also detected after 4000 s at 600 °C (Fig. 5.7d, e). The composition of these particles is also consistent with molybdenum rich particles (Table 5.2).

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(b)

(c)

Fig. 5.5: Carbon extraction replica micrographs showing the identification of grain boundary carbide precipitate in specimen tempered at 600 °C for 2000 s. (a) Bright field, (b) dark field and (c) corresponding selected area diffraction pattern.



(b)

Fig. 5.6: Replica electron micrograph showing that precipitation of cementite after 2000 s of tempering at 600 °C. Most of the carbides formed at the prior austenite boundaries.



(a)



(b)

(c)

Fig. 5.7: Continued .....

The molybdenum content of the carbides appeared to increase with tempering time although this would have to be confirmed by more experiments. The number density of  $Mo_2C$  type precipitates increased with further tempering, at the expanse of cementite (Fig. 5.8).



Fig. 5.8: Micrograph showing substantial nucleation of  $Mo_2C$  precipitate within bainitic ferrite in specimen tempered for 8000 s at 600 °C.



(d)



(e)

Fig. 5.7: (a) Replica electron micrograph showing the precipitation of  $Fe_3C$  after 4000 s of tempering at 600 °C. (b) Bright field from a  $Fe_3C$  particle and (c) corresponding diffraction pattern. (d) Bright field of a  $Mo_2C$  precipitate and (e) corresponding diffraction pattern.

TEMPERING OF BAINITE

Some  $M_6C$  carbide was also found to form after prolonged annealed (Fig. 5.9), the  $M_6C$  have a lower molybdenum concentration relative to the  $Mo_2C$ .



Fig. 5.9: Carbon extraction replica micrograph and corresponding diffraction pattern of a  $M_6C$  precipitate in specimen tempered at 600 °C for 16 hr.

### 5.2.3 Microanalysis of Precipitates

The identification of carbides were carried out using EDX X-ray analysis and selected area electron diffraction patterns. For this purpose a large number of electron diffraction patterns were taken and indexed to characterise the crystal structures of carbides. Chemical compositions of the precipitates were determined using energy dispersive X-ray analysis carried on carbon extraction replicas. These are given in Table 5.1 as a function of time. It can be seen that accelerating tempering has produced considerable variations in the compositions of the carbides.

Table 5.1: Chemical composition of carbides determined by using energy dispersive X-ray analysis as a function of tempering time all specimens tempered at  $620 \, ^{\circ}C$ .

Tempering	Chemical C	Composition	(wt. %)	Precipitate	
Time	Fe	Mn	Mo		
2000 s	93.4	6.54	0.06	$\mathrm{Fe}_{3}\mathrm{C}$	
2000 s	68.57	31.13	0.29	$\mathrm{Fe}_{3}\mathrm{C}$	
4000 s	64.55	< 0.1	35.45	$M_6C$	
4000 s	93.45	6.54	< 0.1	$\mathrm{Fe}_{3}\mathrm{C}$	
4000 s	32.25	5.55	62.19	$Mo_2C$	
4000 s	99.2	0.25	0.55	$\mathrm{Fe}_{3}\mathrm{C}$	
8000 s	17.87	< 0.1	82.13	$Mo_2C$	
8000 s	82.49	17.51	< 0.1	$\mathrm{Fe}_{3}\mathrm{C}$	
16 hr	35.06	3.02	61.91	$M_6C$	
16 hr	48.05	12.54	39.42	$M_6C$	
16 hr	37.6	3.15	59.25	$M_6C$	
16 hr	2.09	2.344	96.58	$Mo_2C$	
31 days	58.80	35.80	5.92	$\mathrm{Fe}_{3}\mathrm{C}$	
$31 \mathrm{~days}$	28.33	4.58	67.10	$Mo_2C$	
31 days	5.12	2.41	92.40	$Mo_2C$	
31 days	26.92	8.21	64.87	$M_6C$	
$31 \mathrm{~days}$	56.92	34.78	8.312	$\rm M_6C$	

## 5.2.4 Effect of Tempering Time on Sub-Unit Morphology

Fig. 5.10-14. illustrate the effect of tempering time on the shape of the bainitic ferrite sub-unit. Fig. 5.10a shows the nucleation of bainite sheaves from the prior austenite grain boundary. It can seen from the micrographs in Fig. 5.10 that there is some tendency for "spheroidisation" after tempering for 2000 s; the tips of the ferrite sub-units beginning to become round.



Fig. 5.10: TEM micrographs showing the effect of short time tempering on the ferrite sub-units. (a) Tempered at 600 °C for 2000 s. (b) Tempered at 600 °C for 4000 s.

(a)

Prolonged annealing continues to produce spheroidisation, as illustrated in Figs. 5.13 and 5.14. It can be seen from the micrograph that the original lenticular subunit morphology with fine tips essentially disappears although a slab shape of ferrite is still maintained. There is some evidence of sub-unit coalescence (Fig. 5.11b); such coalescence seems to occur most rapidly within a given sheaf, presumably because the sub-units are all in interconnected even before annealing. While the broad faces of these sub-units still retain their plate-like shape and this characteristic remains unchanged during tempering for periods of upto 7 days. After that "recrystallisation" started (Fig. 5.13a). It can be observed from the micrograph in Fig. 5.13, that the ferrite formed as result of the decomposition of residual austenite recrystallised first (Fig. 5.13a), while the bainitic ferrite sub-units still retain their parallelism (Fig. 5.13c), but they were ultimately recrystallised after long time *i.e.*, 31 days of tempering (5.14).



Fig. 5.11: TEM thin foil micrographs showing change in ferrite sub-units morphology after tempering for 16 hr at 600 °C. The tips of the sub-units have spheroidised, while their broad faces have altered little and remain more or less parallel to each other.



Fig. 5.12: Micrographs showing microstructure of specimen tempered for 7 days at  $600 \, ^{\circ}C$ . Note that the ferrite sub-units spheroidised but the broad faces still retained their parallel formation.



Fig. 5.13: TEM micrographs showing that specimen partially recrystallised after 18 days of tempering at 600 °C. The ferrite formed as result of tempering of martensite recrystallised, while the sub-units of bainitic ferrite still retained their parallel formation.


Fig. 5.14: Recrystallised microstructure observed in specimen after 31 days of tempering at 600 °C, TEM thin foil micrographs.

## 5.2.5 Decomposition of Retained Austenite

It was surprising to find that some of the original austenite remained untransformed even after annealed at 620 °C for 7 days. This undecomposed austenite transforms to the highly twinned martensite; Fig. 5.15 is a micrograph of the specimen tempered for 7 days at 620 °C, showing the twinned martensite that forms during quenching to ambient temperature. This might have originally been a larger region of relatively low carbon austenite, in which case it would be difficult for it to decompose by the precipitation of carbides.



Fig. 5.15: TEM thin foil micrographs showing that residual austenite (now converted to twinned martensite) is still left undecomposed even after 7 days of tempering at  $600 \, ^{\circ}C$ .

# 5.2.6 Effect of Tempering Time on Bulk Hardness

The hardness level dropped continuously with tempering, with no obvious secondary hardening peak due to the precipitation of carbides. On the other hand, it is likely that the softening was retarded relative to an alloy which did not contain secondary hardening element.



Fig. 5.16: Effect of tempering time on the bulk hardness.

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#### 5.3 Summary

Experiments have been conducted in which mixtures of bainitic ferrite and austenite were tempered at a temperature (620 °C) well above the bainite-start temperature. Annealing caused the tips of the ferrite platelets to round-off, a result which indicate that the original lenticular shape, which is a consequence of the displacive transformation mode, is not the equilibrium shape of the ferrite. The strain energy due to the shape change favours a sharp plate tip since this minimises the strain energy; annealing releases the strain, making way for the plate to adopt a shape more consistent with interfacial energy minimisation. Prolonged annealing also led to a small degree of sub-unit coalescence, the coalescence process being confined to the scale of individual sheaves since the platelets within a given sheaf are from the very beginning of transformation, interconnected. The early stages of tempering lead to the precipitation of cementite, to a small extent at the austenite grain boundaries, but mostly as a consequence of the decomposition of the films of austenite trapped between the ferrite platelets. The precipitation of cementite was eventually followed by that of Mo<sub>2</sub>C carbides, which nucleated independently of the cementite but grew at the expense of cementite. Some  $M_6C$  carbide was also found during long term ageing. Profuse alloy carbide precipitation was eventually accompanied by the further relaxation of the ferrite grains into more equiaxed grains.

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Chapter 5

# Chapter 6 EFFECT OF AUSTENITISATION TEMPERATURE ON THE FORMATION OF BAINITE

Bainite generally adopts a sheaf morphology and these sheaves usually nucleate at the prior austenite grain boundaries. These sheaves grow into the austenite grains until they are stopped by some obstacle such as an austenite grain boundary or another bainite sheaf. Prior austenite grain size can therefore be expected to play an important role in controlling the kinetics of the bainite reaction but there are contradicting results in the literature. This may partly be a consequence of the fact that complex alloy systems were used with several reactions occurring simultaneously, making the interpretation of the experimental data difficult. This chapter is devoted to the study of the effect of austenite grain size on the kinetics of bainitic transformation.

### **6.1 General Introduction**

The usual effect of austenite grain size upon the kinetics of a grain-boundary nucleated transformation, is that of changing the number of nucleation sites per unit volume of sample. As already stated, the available data concerning the effect of austenitising temperature on the kinetics of bainite reaction are conflicting. For example Davenport and Bain [1941] found, using a Fe-0.37C-0.77Mn-0.98Cr (wt. %) steel, that the rate of bainite formation remained unaffected on increasing the austenite grain size from ASTM 7-8 to 2-3§. Similar results were obtained by Allen et al. [1939], who investigated the effect of increasing austenitising temperature on the isothermal transformation of a Fe-1.0Cr (wt. %) steel. They concluded that there is no detectable effect of austenitisation temperature on the subsequent formation of bainite. On the other hand, Hultgren [1947] found that in a series of Mn steels, austenitisation at higher temperatures considerably retarded the decomposition of austenite to bainite, consistent with the earlier work of Winterton [1945]. Cottrell and Ko [1953] investigated the effect of austenitising temperature on a number of Fe-Ni-Mo-Cr hypo-eutectoid low-alloy steels. For reasons which are not clear, they noticed that the rate of bainite reaction in the case of En25 and En26 is increased as the austenitising temperature was raised from 950 °C to 1300 °C, but for En31 steel there was a retardation. Graham and Axon [1953] investigated the

 $<sup>\</sup>S$  ASTM stands for American Society for Testing and Materials.

effects of austenite grain size and austenitisation temperature on the transformation to lower bainite in a Fe-0.97C wt. % alloy. It was claimed that the individual effects of grain size and austenitising temperature were separated. Specimens were austenitised for time periods ranging from 4 to 360 minutes at temperatures of 835, 900 and 990 °C and then fully reacted at 266 °C. It was found that there is an initial decrease in the decomposition rate followed by an increase, as a function of rising austenitising temperature. The initial retardation was attributed to increasing carbide solution, and the subsequent acceleration to the onset of grain growth. In further experiments specimens were austenitised at temperatures ranging from 860 to 990 °C for times chosen to ensure complete carbide solution and to establish a constant grain size of ASTM 6. It was found that the times to 5 % and 95 %reaction at 266 °C increased with increasing austenitising temperature upto about 950 °C, after which the curves flattened out. These results were taken to mean that, upon eliminating the effects due to differing grain sizes and incomplete solution of carbides, in the lower bainite range there remains an effect due to the austenitising temperature. The effect was said to be reversible in a fashion similar to that noted by Cottrell and Ko [1953], but the experimental data presented by Graham and Axon [1959] exhibit a large degree of scatter. Barford et al. [1961] have examined the kinetics of upper an lower bainite in Fe-Mn-C high purity steels using electrical resistivity measurements. They found that the time to any chosen percentage reaction less than 25 % is proportional directly to the mean austenite diameter.

The studies to date are not in general consistent with each other with respect to the austenitising conditions or austenite grain size dependence of the bainite transformation kinetics. This is partly because complex alloy systems were used in which the bainite reaction was sometimes accompanied by other transformations such as the precipitation of carbides or pearlite.

The present work was undertaken in order to study further the effect of austenite grain size on the bainite transformation using alloy systems in which bainitic ferrite growth occurs in isolation.

#### **6.2 Experimental Procedures**

The chemical compositions of the steels used has been given in Table 3.1, they all contain large silicon concentrations to retard the formation of carbides during bainitic transformation.

Cylindrical specimens of 3 mm diameter and 20 mm length, were prepared by

swagging and machining treatments§. All heat treatments were carried out in a Theta industries high speed dilatometer. After homogenisation at 1250 °C for 3 days, specimens were Ni-plated to prevent surface degradation during subsequent heat treatments. Fig. 6.1 shows schematically the heat treatment cycles used.



Fig. 6.1: Schematic representation of the heat treatment cycles used.

The dilatometer was interfaced with a BBC/Acorn computer for data collection. The data were subsequently transferred to an IBM 3087 main frame computer for detailed analysis according to the method described in Chapter 4. The prior austenite grain sizes were measured by sealing polished and unetched specimens in silica tubes, which were evacuated to  $10^{-6}$  torr and sealed off under the partial pressure of dried pure argon gas. The capsules were transferred to the furnace maintained at the austenitisation temperature, austenitised for 5 min in order to thermally groove the austenite boundaries, and then air cooled to ambient temperature.

Conventional metallographic techniques were used for revealing the microstructure. The specimens were etched using 2 % nital solution.

 $<sup>\</sup>S$  The details of the specimen preparation procedures are described in Chapter 3.

## 6.3 Results and Discussion

The micrographs in Fig. 6.2 show a typical bainitic microstructure observed in steels used in the present study. The bainite sheaves nucleate at the prior austenite grain boundaries (Fig. 6.2a) and consisted of much smaller platelets of bainitic ferrite as shown in the TEM micrograph of Fig. 6.2b. No cementite or other carbides detected in the microstructure (Fig. 6.2b).



(a)



(b)

Fig. 6.2: Micrographs showing typical bainitic microstructure in alloy A2. Specimen isothermally transformed at 400 °C for 2000 s after austenitisation at 1200 °C for 5 min. (a) Optical micrograph. (b) TEM micrograph.

## 6.3.1 Transformation in Alloy A2

Fig. 6.3 shows the effect of austenitisation temperature on the kinetics of the bainite reaction. The dilatometric curves indicate that the kinetics are sensitive to austenitisation temperature. In the specimens austenitised at 900 °C, the rate of transformation was found to be much higher than in those austenitised at 1200 °C.



Fig. 6.3: Dilatometric curves showing the effect of austenitisation temperature on the kinetics of bainite reaction in alloy A2.

Fig. 6.4 shows that the length of bainite sheaves is, as expected, also affected by the austenitisation temperature, becoming larger as the grain size increases.



(b)

(a)

Fig. 6.4: Continued.....



(d)

Fig. 6.4: Optical micrographs showing the effect of austenitisation temperature on the microstructure obtained in the alloy A2, by isothermal transformation at 400  $^{\circ}C$  for 2000  $^{\circ}C$  after austenitisation for 5 min at (a) 900  $^{\circ}C$  (b) 1000  $^{\circ}C$  (c) 1100  $^{\circ}C$  and (d) 1200  $^{\circ}C$ .

In order to check whether there is any transformation during cooling from the austenitisation temperature to the isothermal transformation temperature, changes in length were plotted against temperature (Fig. 6.5). No deviation from linearity could be detected, indicating that there is no transformation during cooling to the bainite transformation temperature.



Fig. 6.5: Relative length versus temperature dilatometric curves showing that there is no transformation during cooling prior to the isothermal bainite transformation in alloy A2.



Fig. 6.6: Effect of austenitisation temperature on the volume fraction of bainite in alloy A2. Note that only about 50 % austenite transformed to bainitic ferrite and other left as residual austenite even after longer time.

Fig. 6.6 illustrates the data of Fig. 6.4, after converting the length changes into volume fractions using the methods discussed earlier. The times taken to achieve 5, 50 and 95 % (of the maximum extent at any temperature) of bainite transformation as a function of austenitisation temperature are tabulated in Table 6.2 and plotted in Fig. 6.7.

Table 6.2: Effect of austenitisation temperature on time taken by a fixed amount of bainite transformation in alloy A2.

Austenitisation	Time s		
Temperature <sup>o</sup> C	5 %	50 %	95 %
900	45	135	309
1000	50	146	378
1100	84	321	850
1200	149	374	822



(b)

Fig. 6.7: The effect of austenitisation temperature on the time taken for (a) 5 %, (b) 95 % transformation.

## 6.3.2 Transformation in Alloy A102

The formation of bainite is relatively faster in this alloy because of its lower carbon content. The effect of austenitisation temperature on the kinetics of bainite reaction is shown in Fig. 6.8. Again as the austenitisation temperature increased, the kinetics of the reaction become slower.



Fig. 6.8: Dilatometric curves showing the effect of austenitisation temperature on the kinetics of bainite reaction in alloy A102.

Due to faster bainite reaction kinetics in this alloy, it was necessary to check any transformation happening during cooling. The results shown in Fig. 6.9 and reveal that there is no transformation during cooling except bainite.



Fig. 6.9: Relative length versus temperature dilatometric curves showing that there is no transformation during cooling prior to the isothermal bainite transformation in alloy A102.

The micrographs in Fig. 6.10 show the effect of austenitisation temperature on bainite transformation in alloy A102. Fig. 6.10 again shows, as expected, that the longer sheaves are associated with the higher austenitisation temperatures.



(c)

(b)

(a)

Fig. 6.10: Optical micrographs showing the effect of austenitisation temperature on bainite microstructure in alloy A102. All specimens isothermally transformed at  $480 \degree C$  for 1000 s after austenitisation of 5 min at (a) 900  $\degree C$  and (b) 1000  $\degree C$  and (c) 1200  $\degree C$ .

The amount of bainite formed after austenitisation at different austenitisation temperatures is shown in Fig. 6.11. It is depicted from Fig. 6.11 that the amount of bainite formation also affected, and higher austenitisation temperature leads to the lesser amount of bainite transformation.

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Fig. 6.11: Effect of austenitisation temperature on the volume fraction of bainite obtained in alloy A102. Note that only about 50 % of austenite at most transformed to bainite before the reaction ceased.

The time taken to achieve a fixed amount of bainite transformation was also measured after converting of relative length data to the volume fraction of bainite. The results are given in Table 6.3. Fig. 6.12 show that time taken by 5 and 95 % transformation increases with increasing austenitisation temperature.

Table 6.3: Effect of austenitisation temperature on time taken achieve a fixed amount of bainite transformation in alloy A102.

Austenitisation	Time s		
Temperature <sup>o</sup> C	5 %	95 %	
900	1	60	
1000	4	270	
1100	6	300	
1200	6.5	320	



(a)



(b)

Fig. 6.12: The effect of austenitisation temperature on the time taken by (a) 5 % and (b) 95 % of bainite transformation.

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### 6.3.3 Transformation in Alloy A103

This is the fastest transforming alloy of the three studied, making the study of kinetics rather difficult in this alloy. The optical microstructure is illustrated in Fig. 6.13, and appears different from those of alloys A2 and A102, presumably because a lot more of the austenite transform to bainite.



Fig. 6.13: Optical micrograph showing the morphology of bainite in alloy A103, specimen isothermally transformed to bainite at 530 °C after austenitisation at 1100 °C for 5 min.

The effect of austenitisation temperature on the kinetics of bainite transformation are shown in Fig. 6.14, which shows that there is very little detectable effect of austenitisation temperature on the formation of bainite, simply because the kinetics are so rapid as to mask any grain size effect.



Fig. 6.14: Dilatometric curves showing the effect of austenitisation temperature on the kinetics of bainitic reaction in alloy A103.

It was considered extremely important to determine whether any transformation occurred during cooling from the austenitisation temperature. Fig. 6.15 shows that there is no undesired transformation during cooling. bainite.



Fig. 6.15: Relative length versus temperature dilatometric curves showing that there is no transformation during cooling prior to isothermal transformation in alloy A103.

The micrographs in Fig. 6.16 show the effect of austenitisation temperature in the microstructure, which could be described as "granular" morphology.



(a)

(b)

Fig. 6.16: Optical micrographs showing the effect of austenitisation temperature on bainite microstructure in alloy A103.

## 6.3.4 Austenite Grain Size

Increasing the austenitisation temperature, resulted in a bigger austenite grain size (Figs. 6.17) as measured by using the thermal grooving technique. The grain sizes were measured using the mean lineal intercept (m.l.i) method (Fig. 6.17).



Fig. 6.17: Effect of austenitisation temperature on austenite grain size measured by mean linear intercept method.

### 6.4 Summary

Controlled experiments have been carried out on the influence of austenite grain size on the overall transformation kinetics of the bainite reaction in steels where carbide precipitation (or other reactions) do not accompanying the formation of bainitic ferrite. The primary result is that the reaction rate increases as the austenite grain size is reduced, a result expected in high purity steels where the main site for bainite nucleation is the austenite grain surfaces. The experiments nevertheless needed to be carried out since the published literature conflicting results. A further observation is that the austenite grain size effect might be marked in steels which tend to transform rapidly when compared with the ability of the experimental techniques to resolve the rate of reaction. There are some puzzling observations which need further investigation; Figs. 6.6 and 6.11 indicate that the maximum extent of transformation achieved by prolonged holding at the isothermal reaction temperature, varies with the austenitising temperature. Furthermore, the variation is not systematic, being different for alloy A2 and A102. These results will require further investigation, to confirm the behaviour and to identify the cause. It is speculated that changes in crystallographic texture might tend to make dimensional change a less reliable indicator of the extent of transformation, since a non-random distribution of bainite sheaves could be expected to lead to anisotropic dimensional changes since the invariant plane strain shape change during bainite growth is far from isotropic. In a small grained sample, the anisotropic terms would tend to cancel, bearing just the dilatational components to reflect the extent of reaction.

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EFFECT OF AUSTENITISATION ON BAINITE

# Chapter 7 INTRAGRANULAR NUCLEATION OF BAINITE SHEAVES

### 7.1 Introduction

When austenite decomposes to ferrite, the ferrite is almost always found to nucleate heterogeneously at the austenite grain boundaries, irrespective of the nature of the ferrite transformation products (*i.e.*, allotriomorphic ferrite, Widmanstätten ferrite, pearlite, bainite). Intragranular nucleation is rare indeed in wrought steels. As discussed in the earlier chapter on intragranularly nucleated Widmanstätten ferrite, there are distinct advantages from mechanical properties point of view in industry that intragranular nucleation of ferrite, especially of ferrite plates which otherwise tend to form in packets of parallel plates in identical orientation, packets which do not effectively deflect cleavage cracks.

The purpose of the work presented here was to induce the intragranular nucleation of bainite sheaves by rendering the austenite grains surfaces ineffective by decorating them with thin layer of allotriomorphic ferrite prior to bainite transformation.

#### 7.2 Experimental Procedures

A high-purity high-hardenability Fe-0.12C-2.03Si-2.96Mn (wt. %) alloy was selected, the high silicon in order to retard formation of pearlite, the high manganese contributing towards hardenability, providing an effective means of controlling the thickness of the grain boundary allotriomorphic ferrite.

The material was received in the form of 10 mm diameter bars from which 3 mm diameter cylindrical specimens were prepared by swagging and machining§. All heat treatments, except those for surface relief experiments, were carried out using a Theta Industries high speed dilatometer; the heat treatment cycles used are shown in Fig. 7.1. The samples were nickel plated to approximately 0.08 mm thickness to avoid surface nucleation surface degradation during the heat treatment.

Surface relief experiments were carried out using electrical resistance heating furnaces. After metallographic preparation, the specimens were sealed in silica tubes after flushing several times with high purity argon gas, then evacuating to  $10^{-6}$  torr before finally sealing off with a partial pressure of argon gas§.

 $<sup>\</sup>S$  The details of swagging treatments, specimen preparation and other experimental procedures are described in Chapter 3.



#### Fig. 7.1: Schematic representation of heat treatment cycles used in the present study.

Any surface relief effects were imaged using the Nomarski differential interference technique on a Ziess optical microscope.

## 7.3 Results and Discussion

The time-temperature-transformation diagrams calculated using the method of Bhadeshia [1982] is presented in Fig. 7.2, and the transformation temperatures in Table 7.1.

Table 7.1: Calculated  $Ae_3$ ,  $Ae'_3$ ,  $W_S$ ,  $B_S$ , and  $M_S$  temperatures for the steel used.

	$Ae_3$	$Ae'_3$	$W_S$	$B_S$	$M_S$
Temperature <sup>o</sup> C	812	776	740	520	390



Fig. 7.2: Time-temperature-transformation diagram for the steel used.

In order to eliminate the austenite grain boundary nucleation sites; layers of allotriomorphic ferrite were introduced by isothermal transformation before cooling rapidly into the bainite transformation temperature range. The formation of a uniform layer of the grain boundary allotriomorphic ferrite was a problem due to the relatively fast reaction kinetics and therefore, a series of specimens were isothermally transformed at variety of temperatures for different time periods. Fig. 7.3 shows the results of some of the successful heat-treatments. Austenitisation at 1100 °C for 5 min followed by isothermal transformation at 720 °C for 30 min resulted in fairly uniform and thin layers of grain boundary allotriomorphic ferrite, so that this heat-treatment was selected for further experiments, and that temperature 720 °C is henceforth  $T_1$ .



(b)

Fig. 7.3: Optical micrographs showing the effect of transformation temperature and time on the formation of grain boundary allotriomorphic ferrite. (a) 1100 °C @ 10 min  $\rightarrow$  740 °C @ 3 hr. (b) 1100 °C @ 10 min  $\rightarrow$  720 °C @ 2000 s.

The thickness of grain boundary allotriomorphic ferrite layers as measured on a randomly polished and etched metallographic specimen was around 4-6  $\mu$ m. This left plenty of untransformed austenite available for further intragranularly nucleated bainite transformation at a lower temperature  $T_2$ . The schedule of heat-treatments is presented in Table 7.2

Specimen No.	Heat Treatment
A102AW01	1100 $^{o}$ C @ 10 min $\rightarrow$ 720 $^{o}$ C @ 2000 s
A102AW02	1100 $^{o}$ C @ 10 min $\rightarrow$ 740 $^{o}$ C @ 3 hr
A102AW03	1100 $^{o}$ C @ 10 min $\rightarrow$ 720 $^{o}$ C @ 1000 s $\rightarrow$ 500 $^{o}$ C @ 1000 s
A102AW04	1100 $^{o}$ C @ 10 min $\rightarrow$ 720 $^{o}$ C @ 1000 s $\rightarrow$ 450 $^{o}$ C @ 1000 s
A102AW05	900 $^{o}$ C @ 10 min $\rightarrow$ 720 $^{o}$ C @ 1000 s $\rightarrow$ 450 $^{o}$ C @ 1000 s
A102AW06	1200 $^{o}$ C @ 10 min $\rightarrow$ 720 $^{o}$ C @ 1000 s $\rightarrow$ 450 $^{o}$ C @ 1000 s
A102AW07	1100 $^{o}$ C @ 10 min $\rightarrow$ 720 $^{o}$ C @ 1000 s $\rightarrow$ 450 $^{o}$ C @ 60 s
A102AW08	1100 $^{o}$ C @ 10 min $\rightarrow$ 720 $^{o}$ C @ 800 s $\rightarrow$ 500 $^{o}$ C @ 60 s
A102AW09	1100 $^{o}$ C @ 10 min $\rightarrow$ 720 $^{o}$ C @ 1000 s $\rightarrow$ 540 $^{o}$ C @ 60 s
A102AW10	1100 $^{o}$ C @ 10 min $\rightarrow$ 720 $^{o}$ C @ 400 s $\rightarrow$ 500 $^{o}$ C @ 60 s
A102AW11	1100 $^{o}$ C @ 10 min $\rightarrow$ 720 $^{o}$ C @ 30 min $\rightarrow$ 450 $^{o}$ C @ 1000 s

Table 7.2: Heat treatment schedule.

Fig 7.4 shows the typical microstructure resulting from the two-stage heat treatment. It consists of sheaves of bainite nucleated within the body of the austenite grains and what appears to be thin laths of ferrite nucleated from allotriomorphic ferrite layers. The ferrite laths were in fact found to have a sub-unit type structure on examinations at higher magnifications Fig. 7.5.



Fig. 7.4: Optical micrographs showing the microstructure of the specimen which was isothermally transformed below the  $B_S$  temperature after the formation of grain boundary allotriomorphic ferrite (1100 °C @ 10 min  $\rightarrow$  720 °C @ 30 min  $\rightarrow$  450 °C @ 1000 s).

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Fig. 7.5: Optical micrographs showing the sub-unit type microstructure of the ferrite laths nucleated from grain boundary allotriomorphic (GBA) ferrite. Specimen isothermally transformed at 500 °C for 1000 s after austenitisation at 1100 °C for 10 min and after the formation of GBA layer at 720 °C.

The observation of intragranular nucleation was not completely convincing, so a higher austenitisation temperature  $(1200 \ ^{\circ}C)$  was used to decrease the number density of grain boundary nucleation sites. This resulted in the microstructure shown in Fig. 7.6, where intragranular nucleation has produced a different microstructure in the austenite grain centres composed with that in the vicinity of the grain boundaries.



Fig. 7.6: Optical micrographs showing the microstructure of the specimen which was isothermally transformed below the  $B_S$  temperature after the formation of grain boundary allotriomorphic ferrite. Note the nucleation of bainite sheaves within the body of the prior austenite grain (1200 °C @ 10 min  $\rightarrow$  720 °C @ 1000 s  $\rightarrow$  450 °C @ 1000 s).

The scanning electron micrograph in Figs. 7.7 and 7.8, show more detail from both of the regions. Transmission electron microscopy confirmed that the two kinds of bainite are essentially identical in structure, except for the much larger tendency for the grain boundary nucleated sheaves to ferrite plates (Fig. 7.9).



(a)

(b)

Fig. 7.7: SEM micrographs showing the microstructure of the specimen which was isothermally transformed below the  $B_S$  temperature after the formation of grain boundary allotriomorphic ferrite. Note the nucleation of bainite sheaves within the body of the prior austenite grain. (a) 1200 °C @ 10 min  $\rightarrow$  720 °C @ 1000 s  $\rightarrow$  450 °C @ 1000 s. (b) 1100 °C @ 10 min  $\rightarrow$  720 °C @ 1000 s  $\rightarrow$  500 °C @ 1000 s).



(b)

Fig. 7.8: Micrographs showing the nucleation of bainite sheaves from the grain boundary allotriomorphic ferrite. Note the sub-units structure of bainitic ferrite within the sheaves (1100 °C @ 10 min  $\rightarrow$  720 °C @ 1000 s  $\rightarrow$  450 °C @ 60 s). (a) TEM. (b) Carbon extraction replica.

It was possible using extraction replica (Fig. 7.9) to indentify some of the inclusions which could have served as the required intragranular nucleation sites.

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Fig. 7.9: Replica electron micrographs showing the inclusion assisted nucleation of bainite sheaves (1100 °C @ 10 min  $\rightarrow$  720 °C @ 30 min  $\rightarrow$  450 °C @ 1000 s).
# 7.4 Dilatometry

Dilatometric experiments were carried out to check whether there is any unintended transformation during cooling to the  $B_S$  temperature, which might interfere with the formation of bainite. Fig. 7.10, is a plot of the relative length change versus temperature, the linearity of which demonstrates the absence of any reaction during cooling to the desired isothermal transformation temperatures.

The dilatometric data were converted to volume fractions and Table 7.3 shows the extent of reaction at the isothermal reaction temperatures together with the calculated carbon enrichment in the residual austenite at each stage.

Table 7.3: Measured volume fraction of ferrite and bainite and calculated carbon content of the residual austenite.

Temperature <sup>o</sup> C	Total volume fraction of ferrite	Carbon in residual austenite wt. %
720	$0.117 \pm 0.012$	$0.134 \pm 0.002$
450	$0.354 \pm 0.016$	$0.178 \pm 0.004$

# 7.5 Surface Relief Study

It is well known that displacive reactions cause an invariant-plane strain shape change in the transformed regions. Fig 7.11 shows the surface relief produced on a specimen given the two-stage heat-treatment. It is clear, as expected, that there is no shape change associated with allotriomorphic ferrite growth, whereas there is pronounced relief associated with bainite.



Fig. 7.10: Continued.....



Fig. 7.10: Dilatometric graphs between the relative length change and temperature showing that there is no transformation above the  $B_S$  temperature.



Fig. 7.11: (a) Optical micrographs showing the surface relief produced by bainite sheaves. Note that diffusionally formed allotriomorphic ferrite did not show any surface relief. (b) Optical micrographs of the same specimen in (a) after slight polishing on 6  $\mu$ m diamond paste and etched in 2 % nital solution, showing the underlying microstructure. (1100 °C @ 10 min  $\rightarrow$  720 °C @ 30 min  $\rightarrow$  450 °C @ 1000 s).

### 7.6 Summary

A clear change in microstructure has been observed when the austenite grains boundaries are prevented from nucleating bainite, by covering them with thin layers of allotriomorphic ferrite. When specimens partially transformed to allotriomorphic ferrite are then held at a temperature below  $B_S$ , bainite sheaves nucleate intragranularly, probably on non-metallic inclusions present in steel, although the details required further investigation. However, it is found that some of the allotriomorphs, presumably those which have a favoured orientation relationship (i.e., K-S or N-W type) with the austenite, do develop into packets of parallel sheaves of bainite. This is unlike the behaviour noted when Widmanstätten ferrite is induced to form in samples partially transformed to allotriomorphic ferrite, presumably because the larger undercooling needed to produce bainite allows the barriers (to transformation) presented in the carbon-enriched region near the allotriomorphic ferrite layers can be overcome by the accompanying larger driving force. The effects of bainite nucleation on allotriomorphs can be mitigated by increasing the austenite grain size, but the microstructural changes associated with intragranularly nucleated bainite are nevertheless rather less spectaculated when compared with the intragranularly nucleated Widmanstätten ferrite.

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# <u>Chapter 8</u> ASPECTS OF THE NUCLEATION OF WIDMANSTÄTTEN FERRITE

#### 8.1 Significance of Widmanstätten Ferrite

The requirement for ever increasing toughness in steels has placed restrictions on the use of carbon and other alloying additions, thereby resulting in the development of the "high-strength low-alloy" steels. These steels, used in applications where weld ability and formability are of paramount importance, invariably have a very low carbon content (< 0.1 wt %). The total alloy concentration is usually less than 3.0 wt. %. One of the major problems with their development is the steel used for the weld deposits themselves, which sometimes contain undesirable quantities of Widmanstätten ferrite.

Widmanstätten ferrite is an undesirable constituent and its presence leads to poor toughness in low-alloy steels [Savage and Aaronson, 1966; Garland and Kirkwood, 1975; Rodrigues and Rogerson, 1977]. The long plate-like morphology so characteristic of Widmanstätten ferrite offers little resistance to cleavage crack propagation when present in packets of parallel plates (Fig. 8.1); it has been suggested that this is because the packets offer a larger effective grain size, although the details are not clear [Widgrey, 1975; Fick and Rogerson, 1977; Billy *et al.* 1980]. The plates in individual packets are in identical orientation in space.

The problem of the unwanted Widmanstätten ferrite is particularly acute in steel weld deposits, where it is impractical to modify the microstructure which evolves during solidification and during subsequent cooling to ambient temperature, by the sort of thermomechanical processing normally used to refine the microstructure in wrought alloys. Consequently, the main avenue available for the minimisation of the quantity of Widmanstätten ferrite is alloy design, and this in turn requires a good knowledge of the factors controlling its nucleation and growth.

# 8.1.1 Scope and the Problem

The growth of Widmanstätten ferrite is reasonably well understood and the lengthening rate of an individual Widmanstätten ferrite plate can be predicted with a fair accuracy, as a function of alloy chemistry and temperature by using currently available carbon diffusion-controlled growth rate models for Widmanstätten ferrite [Bhadeshia, 1982; 1985; 1985b]. However, less attention has been given to the nucleation of Widmanstätten ferrite. The following chapter is devoted to the study of some aspects the nucleation of behaviour of Widmanstätten ferrite. The problem is examined theoretically in the context of a displacive transformation mechanism and is assessed against both previously available and new experimental data obtained in the present study.



Fig. 8.1: Micrograph showing Widmanstätten ferrite formed in a Fe-0.4C-2.04Si (wt.%) alloy isothermally transformed at 680 °C for 5 min after austenitisation at 1300 °C for 30 min. Note that the parallel formation of Widmanstätten ferrite plates from the grain boundary allotriomorph of ferrite.

#### 8.2 Nucleation

Nucleation, classically arises because of the net increase in free energy caused by the formation of a small amount of product phase, since the new particle has during the early stages of transformation, a large surface/volume ratio. During the growth stage on the other hand, a negligible amount of the available free energy is dissipated in the creation of new surface.

#### 8.2.1 Classical Nucleation Theory

The basis of the classical theory of nucleation originated by Volmer and Weber [1926] and Becker and Döring [1935] is to assume that embryos are internally uniform and have the same structure, composition and properties as the final product phase in bulk form. These assumptions leave the shape and size of the embryo as the only variable parameter. The shape is that which minimizes the free energy of formation. The free energy change during the formation of a nucleus consists of: a) the energy of the interface, b) elastic strain energy due to any volume change, and c) strain energy associated with the lattice distortion produced by partial or complete coherency between two lattices. On the basis of the assumption of isotropy and the absence of strain, the nucleus may be taken to grow from a spherical embryo. Thus the Gibbs free energy for the formation of a spherical embryo of radius r is given by:

$$\Delta G = \left(\frac{4}{3}\right)\pi r^3 \Delta G^{chem} + 4\pi r^2 \sigma \tag{8.1}$$

and the relationship between  $\Delta G^{chem}$  and r will have the form shown in Fig. 8.2a. The growth of embryos smaller than the critical radius  $r^*$  leads to an increase in the free energy and thus there is a greater tendency for such embryos to shrink rather than grow. Embryos larger than  $r^*$  are stable because their growth is accompanied by a decrease in  $\Delta G^{chem}$ , embryos of radius  $r^*$  are unstable having an equal chance of shrinking or growing. Therefore, the condition for the continued growth of an embryo is that the radius should exceed  $r^*$ , where  $d\Delta G/dr = 0$  i.e.

$$r^* = \frac{2\sigma}{(-\Delta G^{chem})} \tag{8.2}$$

and the critical free energy, or activation energy barrier for nucleation, is given by

$$\Delta G^* = \frac{16\sigma^3}{3(\Delta G^{chem})^2} \tag{8.3}$$

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 $\Delta G^{chem}$  is strongly temperature-dependent as shown in Fig. 8.2b, so the temperature dependence of  $r^*$  and  $\Delta G^*$  may be assessed in terms of the temperature dependence of  $\Delta G^{chem}$ . A steady-state nucleation rate N may be defined as the number of stable nuclei produced in a unit time in a unit volume of untransformed solid, and N is proportional to  $exp(-\frac{\Delta G^*}{RT})$ . The rate at which individual nuclei grow will also be dependent on the frequency with which atoms adjacent to the nucleus can join it and this will be proportional to  $exp(-\frac{\Delta G^*}{RT})$ , where  $\Delta G^*_d$  is the free energy of activation for diffusion. One may therefore write a simplified representation of the rate of nucleation of a precipitate as:

$$N \propto exp[-(\frac{k\sigma^3}{|\Delta G^{chem}|^2} + \Delta G_d^*)/RT]$$
(8.4)

where k is a geometrical constant. It follows that

$$N \propto \nu \ exp(-\frac{\Delta G^*}{RT})$$
 (8.5)

where  $\nu$  is pre-exponential attempt frequency factor and  $\Delta G^*$  is an effective activation energy.

#### 8.2.2 Isothermal Nucleation of Martensite

Theories of martensitic nucleation designed to account for the observed transformation kinetics, are largely concerned with initial growth of an existing martensitic embryo, which nucleated by faulting, from a group of existing dislocations [Olson and Cohen, 1976]. The fault energy  $\gamma$  per unit area associated with such embryo, *n* atomic planes in thickness, can be expressed as:

$$\gamma = n\rho_A(\Delta G^{chem} + E^{str}) + 2\sigma n \tag{8.6}$$

Where  $\rho_A$  is the density of atoms in a close-packed plane, in moles per unit area,  $\Delta G^{chem}$  and  $E^{str}$  are parent/product chemical free energy difference and coherency strain energy respectively, expressed as molar quantities, and  $\sigma_n$  is the particle/matrix interfacial energy (per unit area). If a stress  $\tau$  is required to move an array of n dislocations of Burgers vector **b**, then the work done in creating a fault of energy  $\gamma$  is given by:



(a)



(b)

Fig. 8.2: (a) Schematic illustration of the relationship between free energy and radius of embryo r. (b) Schematic representation of the temperature dependence of Gibbs free energy [Bruke, 1965].

$$\gamma = -n\tau \mathbf{b} \tag{8.7}$$

In the theory of thermally activated deformation, the activation energy  $\Delta G^*$  for dislocation motion under an applied stress  $\tau$  is expressed as [Conrad, 1964; Dorn, 1968]:

$$\Delta G^* = \Delta G_o^* - (\tau - \tau_\mu) V^* \tag{8.8}$$

Where  $\Delta G_o^*$  is the activation energy in the absence of applied stress,  $\tau_{\mu}$  is the athermal resistance to dislocation motion, and  $V^*$  is the activation volume, as measured from deformation experiments. The expression for isothermal martensitic nucleation can be obtained by substitution of Eqs. 8.6 and 8.7 into Eq. 8.8:

$$\Delta G^* = \Delta G_o^* + [\tau_\mu + (\frac{\rho_A}{\mathbf{b}})E^{str} + \frac{2\sigma}{n\mathbf{b}}]V^* + [(\frac{\rho_A}{\mathbf{b}})V^*]\Delta G^{chem}$$
(8.9)

According to Eq. 8.9, the activation energy for isothermal martensitic nucleation should therefore vary linearly with the chemical driving force if  $V^*$  remains constant. As demonstrated by Fig. 8.3, a straight line relationship is found between the activation energy and the driving force for the Fe-Ni-Mn systems [Pati and Cohen, 1971].

### 8.3 Variation of Driving Force with Temperature

The driving force for the nucleation of a phase varies with temperature. If the driving force is calculated assuming that it gives a certain constant detectable nucleation rate N, irrespective of the steel used, then through the classical nucleation theory (Eq. 8.5):

$$N = \nu \ exp[\frac{-\Delta G^*}{RT}] \tag{8.10}$$

so that

$$\Delta G^* = RT ln[\frac{N}{\nu}] \tag{8.11}$$

or

$$-\Delta G^* = \beta T \tag{8.12}$$

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Fig. 8.3: Variation of activation free energy with the driving force in Fe-Ni-Mn systems [after Pati and Cohen, 1971].

where  $\nu$  is pre-exponential attempt frequency factor, R is the gas constant and  $\beta = Rln[\frac{N}{\nu}].$ 

It follows that  $\beta$  is a constant, since N is a constant irrespective of the steels used.  $\beta$  is expected to be negative, since the nucleation rate should always be less than the attempt frequency.

Now according to the theory of isothermal nucleation of martensite, a linear dependence of activation energy on the chemical driving force [Magee, 1970, Raghavan - 143 -

and Cohen, 1971, Olson and Cohen, 1976]:

$$\Delta G^* = \lambda_1 \Delta G_{B_S}^{\gamma \to \gamma' + \alpha} + \lambda_1 E^{str} + \lambda_2 \sigma + \lambda_3 \tag{8.13}$$

where

 $\lambda_1 = (\rho_A/\mathbf{b})V^*; \ \lambda_2 = (2V^*/(n\mathbf{b}); \ \lambda_3 = \Delta G_o^* + \tau \mu V^*, \ \text{and} \ \Delta G_{B_S}^{\gamma \to \gamma' + \alpha} = \Delta G^{chem}.$ where  $\lambda_1 \to \lambda_3$  are constants characteristic of the lattice and of the nucleus,  $E^{str}$  is the strain energy per unit volume of the nucleus and  $\sigma$  is the interfacial energy per unit area. According to Eq. 8.13 a linear dependence of activation free energy on temperature *i.e.*,  $-|\Delta G_{B_S}^{\gamma \to \gamma' + \alpha}| \propto T$  is expected if the reaction followed the isothermal martensitic nucleation kinetics.

### 8.4 Nucleation of Widmanstätten Ferrite and Bainite

It is unlikely that the nucleation of Widmanstätten ferrite and bainite can be described in terms of classical nucleation theory, since it appears that the activation energy for its nucleation is a linear function of the transformation temperature [Bhadeshia, 1981]. This behaviour can be explained using the theory of isothermal martensitic nucleation. The thermodynamics of bainite nucleation are not established beyond doubt, but evidence suggests that the formation of a nucleus involves the diffusion of carbon, so that the nucleus that forms has the composition giving the maximum free energy change on formation from austenite. This was established by an analysis of time-temperature-transformation (TTT) diagrams of low alloy steels [Bhadeshia, 1982].

#### **8.4.1** The Driving Force for the Nucleation

The change in free energy during the austenite/ferrite ( $\gamma / \alpha$ ) phase transformation is shown schematically in Fig. 8.5. The free energy required for the nucleation of ferrite can be obtained by constructing parallel tangents. The parallel tangent construction is consistent with the formation of a nucleus whose composition is such that the maximum value of  $G_{max}$  is obtained [Hillert, 1953], hence this probably represents the most likely composition of the nucleus, although such a criterion does not exclude the formation of nucleus of other compositions. The use of the nucleus composition corresponding to the maximum  $G_{max}$  should be a good approximation for steels, since the solubility of carbon in ferrite is so limited that any carbon concentration up to the equilibrium level makes negligible difference to the magnitude of  $G_{max}$ . Numerical values of  $G_{max}$  can be obtained by solving the following equations simultaneously [Bhadeshia, 1982]:

$$G_{Fe}^{\gamma \to \alpha} + RTln[\frac{a_{Fe}^{\alpha}(1 - x_{\alpha}^{\alpha\gamma})}{a_{Fe}^{\gamma}(1 - x_{\gamma}^{\gamma\alpha})}] - RTln[\frac{a_{c}^{\alpha}(x_{\alpha}^{\alpha\gamma})}{a_{c}^{\gamma}(x_{\gamma}^{\gamma\alpha})}] = 0$$
(8.14)

$$G_{max} = RTln[\frac{a_c^{\alpha}(x_{max})}{a_c^{\gamma}(\overline{x})}] = 0$$
(8.15)

where  $a_{Fe}^{\alpha}(1-x)$  refers to the activity of iron in ferrite evaluated at the concentration (1-x), and a similar rationale applies to the other activity terms. The term  $G_{Fe}^{\gamma \to \alpha}$  refers to the free energy change accompanying the  $\gamma \to \alpha$  transformation in pure iron and R is the gas constant. The term  $\overline{x}$  is the average carbon concentration of the steel concerned and  $x_{max}$  represents the composition of ferrite which satisfies equation 8.14.



Fig. 8.4: Schematic diagram illustrating the driving forces required for the nucleation  $(G_{max})$  and growth  $(\Delta G^{\gamma \to \gamma' + \alpha})$  of Widmanstätten ferrite from austenite.

#### 8.5 Determination of the Energy Function

Bhadeshia [1981] has demonstrated that the nucleus for Widmanstätten ferrite and bainite is identical, even though the respective growth mechanisms differ. The activation energy for nucleation varies directly with the driving force, consistent with a displacive nucleation mechanism. The redistribution of carbon is a thermodynamic necessity during the nucleation process for Widmanstätten ferrite of bainite. Using this assumption, a method has been developed which gives an indication of the amount of free energy necessary in order to ensure a detectable nucleation rate for the Widmanstätten ferrite and bainite transformations.

It is well known that in low-alloy steels a pronounced bay appears in the timetemperature-transformation (TTT) diagram. This bay is taken to correspond with the interpretation of two 'C'-curves, used for reconstructive and other displacive reactions. The top of the lower C curve is usually identified with the bainite-start  $(B_S)$  temperature, although it could correspond to the onset of Widmanstätten ferrite transformation. Hence, the upper part of the displacive C curve temperature is that at which ferrite first forms with an IPS shape change. This is confirmed by detailed studies of Fe-Mn-Si-C steels [Bhadeshia and Edmonds, 1979].

The experimental data of BISRA [1956a] were chosen for analysis because this is one of the more meticulously determined sets of TTT curves. The list of steels utilized in this investigation is given in Table 8.1. These data were used to calculate the free energies available during nucleation under two circumstances:

- a) under the assumption that the ferrite nucleates with the parent austenite carbon content.
- b) that there is partitioning of carbon during nucleation.

Since the existence of two separable C curves is the basis of the analysis, only those TTT diagrams [BISRA, 1956b] whose component curves could be readily distinguished were used initially although the results were subsequently applied indiscriminately.

#### 8.5.1 Details of the Thermodynamic Calculations

The thermodynamic methods used are based on the Lacher [1973] and Fowler and Guggenheim [1939] formalisms, as first applied to steels by Aaronson *et al.* [1966a, b] This work was later corrected and reassessed by Shiflet *et al.* [1973], whose derivations are used throughout the present work but with following modifications:

• To equations modified by Bhadeshia [1981b] in order to allow for the high level

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of carbon in the supersaturated ferrite, and to take account for Zener ordering.

• Partial molar enthalpies  $\Delta \overline{H}_{\gamma}$  and excess partial molar entropy  $\Delta \overline{S}_{\gamma}$  of solution of carbon in austenite are taken to be functions of carbon content. The temperature dependence [Lobo and Geiger, 1976a; 1976b] of  $\Delta \overline{H}_{\alpha}$  and  $\Delta \overline{S}_{\alpha}$  is also taken into account.

Other thermodynamic data needed for the calculations are listed in references. [Bhadeshia, 1981b, Bhadeshia, 1980, Kaufman and Clougherly, 1963]. The Zener ordering energies were calculated as in references. [Fisher, 1949, Zener, 1946]. A FORTRAN IV computer program due to Bhadeshia [1981], capable of doing all the necessary calculations (with the input of steel composition) was utilised in the present analysis.

#### 8.6 Results and Discussion

#### **8.6.1** Energy Functions

The results of the analysis of experimental data of BISRA [1956b] are plotted in Fig. 8.5 and Fig. 8.6, from which it seems that the formation of a nucleus with the equilibrium carbon content is the true circumstance; the alternative hypothesis would lead to nucleation against a positive driving force for a few of the steels examined. Intuitively, the formation of a nucleus with an equilibrium carbon content seems more reasonable (irrespective of the carbon content of the ferrite at the growth stage) if it is considered that the thermally activated development of an embryo to the critical nucleus size occurs through a large number of small scale fluctuations, rather than a sudden large fluctuation. Under these circumstances the rejection of few carbon atoms that would be expected within the critical nucleus volume should be readily feasible.

#### 8.6.2 Further Analysis of the Thermodynamic Data

In order to check the hypothesis that the nucleation of Widmanstätten ferrite and bainite is similar, it was decided to carry out a further analysis of the published experimental data [BISRA, 1956b], following the same method as described in the preceding section except now taking into account of the stored energy of Widmanstätten ferrite or bainite.



Fig. 8.5: Curves representing the free energy change necessary in order to obtain a detectable growth rate of ferrite. (a) The case when the free energy change is calculated on the basis that ferrite inherits the parent austenite carbon content. (b) When the ferrite forms with the equilibrium or para-equilibrium carbon content.

No	Steels	$B_S$	$G_{max}$	$G^{\gamma  o lpha_s}$	$G^{\gamma \to \alpha_s}$ Chemical Composition				sitior	1		
		°C	$\rm J~mol^{-1}$	$\rm J~mol^{-1}$				(wt.	%)			
					$\mathbf{C}$	Si	Mn	Ni	Mo	$\operatorname{Cr}$	others	3
1	En-13	600	-348	-128	0.19	0.14	1.37	0.56	0.39	0.21	Ae3 - 793	Ac3 774
2	En-16	580	-421	-27	0.33	0.18	1.48	0.26	0.27	0.16	- 170	749
3	En-17	550	-562	-18.	0.38	0.25	1.49	0.24	0.41	0.14	- 764	740
4	En-18	560	-548	41	0.48	0.25	0.86	0.18	0.04	0.98	- 753	734
5	En-18	560	-581	-97	0.39	0.16	0.89	0.25	0.00	0.88	- 764	747
6	En-19	540	-626	-98	0.41	0.31	0.64	0.81	0.30	1.24	-760	740
7	En-19	570	-546	-49	0.41	0.23	0.67	0.21	0.23	1.01	-768	753
8	En-22	540	-471	42	0.40	0.26	0.62	3.45	0.10	0.28	- 720	700
9	En-23	500	-687	-224	0.33	0.23	0.57	3.26	0.09	0.85	-	
10	En-23	520	-596	-154	0.32	0.28	0.61	3.22	0.22	0.63	-	
11	En-24	530	-634	-133	0.38	0.20	0.69	1.58	0.26	0.95	- 749	725
12	En-24	530	-662	-186	0.36	0.22	0.52	1.52	0.27	1.17	-	
13	En-25	510	-726	-279	0.32	0.27	0.56	2.37	0.51	0.74	-	
14	En-25	500	-754	-308	0.31	0.20	0.62	2.63	0.58	0.64	-	
15	En-26	520	-642	-130	0.38	0.15	0.56	2.42	0.46	0.74	-737	710
16	En-26	480	-823	-206	0.42	0.31	0.67	2.53	0.48	0.72	- 73	2 700
17	En-28	440	-946	-444	0.32	0.19	0.51	3.02	0.48	1.37	0.18V	
18	En-28	470	-818	-441	0.25	0.15	0.52	3.33	0.65	1.14	0.16V	
19	En-30A	420	-979	-412	0.35	0.14	0.44	4.23	0.13	1.43	-	
20	En-30B	420	-1007	-488	0.32	0.29	0.47	4.13	0.30	1.21	_	

Table 8.1: List of chemical compositions of steels, and calculated free energy data.

Table 8.1: Continued .....

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Steels	$B_S$	$G_{max}$	$G^{\gamma  o lpha_s}$	Chemical Composition							
	°C	$\rm J~mol^{-1}$	$\rm J~mol^{-1}$				(wt.	%)			
				С	Si	Mn	Ni	Mo	$\mathbf{Cr}$	others	
En-40B	450	-1007	-602	0.26	0.21	0.55	0.25	0.54	3.34	-785	770
En-47	560	-575	49	0.51	0.27	0.72	0.15	0.05	0.94	-752.4	734
En-100	520	-640	-109	0.40	0.21	1.32	1.03	0.22	0.53	- 745	715
En-110	520	-704	-180	0.39	0.23	0.26	1.44	0.18	1.11	-757	741
En-110	520	-686	-98	0.44	0.23	0.58	1.40	0.11	1.26	-743	720
En-35	640	-308	-53	0.24	0.17	0.42	1.84	0.20	0.18	-779	762
En-36	550	-444	-259	0.14	0.19	0.46	3.55	0.12	1.11	-760	724
En-36	580-	-362	-181	0.15	0.25	0.41	3.02	0.15	0.90	-	
En-38	550	-425	-383	0.11	0.21	0.31	5.04	0.30	0.13	-	
En-38B	500	-633	-419	0.15	0.21	0.38	4.33	0.17	1.16	-	
En-320	520	-644	-450	0.14	0.22	0.50	2.13	0.18	2.00	- 779	756
En-354	530	-620	-356	0.19	0.21	0.90	1.87	0.81	1.08	- 776	749
En-31	530	-466	000	1.08	0.25	0.53	0.33	0.06	1.46	-	
En-39A	540	-435	-288	0.11	0.09	0.38	4.15	0.07	1.33	-	
En-355	520	-655	-377	0.20	0.23	0.61	2.00	0.19	1.65	-	
En-14	560	-525	-163	0.29	0.26	1.27	0.21	0.04	0.12	-	
En-21	570	-320	11	0.33	0.23	0.74	3.47	0.00	0.07	-	
En-111	600	-360	40	0.35	0.13	0.65	1.27	0.00	0.55	-	
En-325	620	-237	-52	0.20	0.11	0.53	1.75	0.25	0.50	-	
En-352	600	-384	-153	0.20	0.15	0.71	1.13	0.05	0.80	-	
En-353	560	-500	-273	0.18	0.26	0.73	1.34	0.11	1.11	-	
En-20	600	-461	-149	0.27	0.13	0.60	0.19	0.55	0.74	-	
En-20	500	-891	-316	0.41	0.23	0.58	0.15	0.74	1.39	-	
	Steels En-40B En-47 En-100 En-110 En-110 En-35 En-36 En-36 En-38 En-38B En-38B En-320 En-354 En-31 En-31 En-354 En-354 En-355 En-14 En-21 En-21 En-21 En-352 En-352 En-353 En-353	Steels       B_S °C         En-40B       450         En-47       560         En-100       520         En-110       520         En-110       520         En-35       640         En-36       550         En-38       550         En-38       500         En-38       500         En-38       500         En-38       530         En-38       530         En-31       530         En-354       530         En-354       520         En-354       530         En-355       520         En-354       530         En-355       520         En-354       520         En-355       520         En-355       520         En-355       520         En-111       600         En-325       620         En-352       620         En-353       560         En-353       560         En-353       560         En-320       600         En-320       600         En-353       560 <td>Steels       <math>B_S</math> °C       <math>G_{max}</math> J mol<sup>-1</sup>         En-40B       450       -1007         En-47       560       -575         En-100       520       -640         En-110       520       -704         En-110       520       -686         En-310       520       -686         En-35       640       -308         En-36       550       -444         En-36       580-       -362         En-38       550       -425         En-38       500       -633         En-38B       500       -633         En-38B       500       -644         En-37       520       -644         En-38B       530       -620         En-37       530       -620         En-31       530       -425         En-355       520       -655         En-355       520       -525         En-14       560       -525         En-111       600       -360         En-352       620       -237         En-353       560       -500         En-353       560       -500</td> <td>Steels<math>B_S</math> °C<math>G_{max}</math> I mol<sup>-1</sup><math>G^{\gamma \rightarrow \alpha_s}</math> J mol<sup>-1</sup>En-40B<math>450</math><math>-1007</math><math>-602</math>En-47<math>560</math><math>-575</math><math>49</math>En-100<math>520</math><math>-640</math><math>-109</math>En-110<math>520</math><math>-704</math><math>-180</math>En-110<math>520</math><math>-686</math><math>-98</math>En-310<math>520</math><math>-686</math><math>-98</math>En-35<math>640</math><math>-308</math><math>-53</math>En-36<math>550</math><math>-444</math><math>-259</math>En-36<math>580</math><math>-362</math><math>-181</math>En-38<math>550</math><math>-425</math><math>-383</math>En-38<math>500</math><math>-633</math><math>-419</math>En-38<math>500</math><math>-644</math><math>450</math>En-38<math>530</math><math>-620</math><math>-356</math>En-31<math>530</math><math>-644</math><math>-288</math>En-31<math>530</math><math>-466</math><math>000</math>En-35<math>520</math><math>-655</math><math>-377</math>En-14<math>560</math><math>-525</math><math>-163</math>En-35<math>520</math><math>-360</math><math>40</math>En-31<math>570</math><math>-320</math><math>11</math>En-111<math>600</math><math>-360</math><math>40</math>En-325<math>620</math><math>-237</math><math>-52</math>En-352<math>600</math><math>-384</math><math>-153</math>En-353<math>560</math><math>-500</math><math>-273</math>En-20<math>600</math><math>-461</math><math>-149</math></td> <td>Steels         <math>B_S</math> °C         <math>G_{max}</math> <math>G^{\gamma \rightarrow \alpha_s}</math> J mol<sup>-1</sup>         J mol<sup>-1</sup>           En-40B         450         -1007         -602         0.26           En-40B         560         -575         49         0.51           En-400         520         -640         -109         0.40           En-100         520         -640         -109         0.40           En-110         520         -704         -180         0.39           En-110         520         -686         -98         0.44           En-35         640         -308         -53         0.24           En-36         550         -444         -259         0.14           En-36         550         -425         -383         0.11           En-38         500         -633         -419         0.15           En-38         500         -644         -4500         0.14           En-38         500         -620         -356         0.19           En-31         530         -620         -356         0.19           En-31         530         -625         -377         0.20           En-355         520         -65</td> <td>Steels         <math>B_S</math> °C         <math>G_{max}</math> J mol<sup>-1</sup> <math>G^{\gamma \rightarrow \alpha_*}</math> J mol<sup>-1</sup>         Ch           En-40B         450         -1007         -602         0.26         0.21           En-40B         560         -575         49         0.51         0.27           En-407         560         -575         49         0.40         0.21           En-100         520         -640         -109         0.40         0.23           En-110         520         -704         -180         0.39         0.23           En-110         520         -686         -98         0.44         0.23           En-35         640         -308         -53         0.24         0.17           En-36         550         -444         -259         0.14         0.19           En-38         550         -425         -383         0.11         0.21           En-38         500         -633         -419         0.15         0.21           En-38         500         -644         -450         0.14         0.22           En-38         500         -620         -356         0.19         0.21           En-355         520         &lt;</td> <td>Steels         <math>B_S</math> °C         <math>G_{max}</math> <math>G^{\gamma \rightarrow \alpha}</math>         Chemical Steels           °C         J mol<sup>-1</sup>         J mol<sup>-1</sup>         J mol<sup>-1</sup>         J mol<sup>-1</sup>           En-40B         450         -1007         -602         0.26         0.21         0.55           En-47         560         -575         49         0.51         0.27         0.72           En-100         520         -640         -109         0.40         0.21         1.32           En-110         520         -646         -180         0.39         0.23         0.26           En-110         520         -686         -98         0.44         0.23         0.58           En-35         640         -308         -53         0.24         0.17         0.42           En-36         550         -444         -259         0.14         0.19         0.44           En-38         550         -425         -383         0.11         0.21         0.38           En-38         500         -633         -419         0.15         0.21         0.39           En-38         500         -620         -356         0.14         0.22         0.50      <tr< td=""><td><math display="block"> \begin{array}{cccccccccccccccccccccccccccccccccccc</math></td><td><math display="block"> \begin{array}{cccccccccccccccccccccccccccccccccccc</math></td><td><math display="block"> \begin{array}{cccccccccccccccccccccccccccccccccccc</math></td><td><math display="block"> \begin{array}{cccccccccccccccccccccccccccccccccccc</math></td></tr<></td>	Steels $B_S$ °C $G_{max}$ J mol <sup>-1</sup> En-40B       450       -1007         En-47       560       -575         En-100       520       -640         En-110       520       -704         En-110       520       -686         En-310       520       -686         En-35       640       -308         En-36       550       -444         En-36       580-       -362         En-38       550       -425         En-38       500       -633         En-38B       500       -633         En-38B       500       -644         En-37       520       -644         En-38B       530       -620         En-37       530       -620         En-31       530       -425         En-355       520       -655         En-355       520       -525         En-14       560       -525         En-111       600       -360         En-352       620       -237         En-353       560       -500         En-353       560       -500	Steels $B_S$ °C $G_{max}$ I mol <sup>-1</sup> $G^{\gamma \rightarrow \alpha_s}$ J mol <sup>-1</sup> En-40B $450$ $-1007$ $-602$ En-47 $560$ $-575$ $49$ En-100 $520$ $-640$ $-109$ En-110 $520$ $-704$ $-180$ En-110 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0.44           En-35         640         -308         -53         0.24           En-36         550         -444         -259         0.14           En-36         550         -425         -383         0.11           En-38         500         -633         -419         0.15           En-38         500         -644         -4500         0.14           En-38         500         -620         -356         0.19           En-31         530         -620         -356         0.19           En-31         530         -625         -377         0.20           En-355         520         -65	Steels $B_S$ °C $G_{max}$ J mol <sup>-1</sup> $G^{\gamma \rightarrow \alpha_*}$ J mol <sup>-1</sup> Ch           En-40B         450         -1007         -602         0.26         0.21           En-40B         560         -575         49         0.51         0.27           En-407         560         -575         49         0.40         0.21           En-100         520         -640         -109         0.40         0.23           En-110         520         -704         -180         0.39         0.23           En-110         520         -686         -98         0.44         0.23           En-35         640         -308         -53         0.24         0.17           En-36         550         -444         -259         0.14         0.19           En-38         550         -425         -383         0.11         0.21           En-38         500         -633         -419         0.15         0.21           En-38         500         -644         -450         0.14         0.22           En-38         500         -620         -356         0.19         0.21           En-355         520         <	Steels $B_S$ °C $G_{max}$ $G^{\gamma \rightarrow \alpha}$ Chemical Steels           °C         J mol <sup>-1</sup> J mol <sup>-1</sup> J mol <sup>-1</sup> J mol <sup>-1</sup> En-40B         450         -1007         -602         0.26         0.21         0.55           En-47         560         -575         49         0.51         0.27         0.72           En-100         520         -640         -109         0.40         0.21         1.32           En-110         520         -646         -180         0.39         0.23         0.26           En-110         520         -686         -98         0.44         0.23         0.58           En-35         640         -308         -53         0.24         0.17         0.42           En-36         550         -444         -259         0.14         0.19         0.44           En-38         550         -425         -383         0.11         0.21         0.38           En-38         500         -633         -419         0.15         0.21         0.39           En-38         500         -620         -356         0.14         0.22         0.50 <tr< td=""><td><math display="block"> \begin{array}{cccccccccccccccccccccccccccccccccccc</math></td><td><math display="block"> \begin{array}{cccccccccccccccccccccccccccccccccccc</math></td><td><math display="block"> 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Fig. 8.6: The change in maximum free energy  $(G_{max})$  required for a detectable nucleation rate of ferrite.

Here our purpose is to test whether it is the same nucleus that develops into  $\alpha_W$  or  $\alpha_b$ , depending on the available driving force. The Steven and Haynes data have been classified, by calculation of available free energy at the highest temperature of the displacive C curve, into steels where top part of the C curve corresponds to  $\alpha_W$  and those where it corresponds to  $\alpha_b$ . Table 8.2 shows this classification respectively. Fig. 8.7 is a plot of driving force  $G_{max}$  vs temperature for both types of steels. These two figures almost having straight line configuration. The slope for Fig. 8.7a was calculated as  $2.56 \pm 0.77$  J mol<sup>-1</sup> °C and for Fig. 8.7b was  $2.78 \pm 0.44$  J mol<sup>-1</sup> °C. The slope of both the curves is within experimental error, the same. These results confirm the previous conclusion that bainite and Widmanstätten ferrite grow from the same nucleus, which has an equilibrium carbon content [Bhadeshia, 1981]. It is possible for the nucleus, can develop into either  $\alpha_W$  or bainite, depending on the driving force available for growth. The free energy available for growth is expected to be enhanced beyond the critical size due to the decreasing contribution of interfacial energy per unit volume, with increasing size.

### **8.6.3** Applications of $G_N$ Curves

Prediction of microstructure is of importance to industry and  $G_N$  curves can be used for example (a) to determine the transition from Widmanstätten ferrite to bainite and (b) to determine the temperature at which Widmanstätten ferrite first formed in a detectable quantity or (c) to predict whether in the steel concerned Widmanstätten ferrite will form or not.

# 8.6.3.1 Transition from Widmanstätten Ferrite to Bainite

The concepts developed earlier may thermodynamically be expressed as follows, supposing

 $G_1$  = Stored energy per mole of Widmanstätten ferrite ( $\alpha_W$ )  $G_2$  = Stored energy per mole of bainite ( $\alpha_b$ )

Table 8.2: Classification of calculated data as Widmanstätten ferrite and bainitic steels (see text).

No.	Steels	B <sub>S</sub> °C	$G_{max}$ J mol <sup>-1</sup>
1	En-13	600	-348
2	En-16	580	-421
3	En-17	550	-562
4	En-18	560	-548
5	En-18	560	-581
6	En-19	540	-626
7	En-19	570	-546
8	En-22	540	-471
9	En-23	500	-687
10	En-23	520	-596
11	En-24	530	-634
12	En-24	530	-662
13	En-25	510	-726
14	En-25	500	-754
15	En-26	520	-642
16	En-26	480	-823
17	En-47	560	-575
18	En-100	520	-640
19	En-110	520	-704
20	En-110	520	-686
21	En-35	640	-308
22	En-36	550	-444
23	En-36	580	-362
24	En-38	550	-425

(a) Widmanstätten ferrite steels.

Table 8.2: Continued .....

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No.	Steels	$B_S$	$G_{max}$
		°C	J mol <sup>-1</sup>
25	En-354	530	-620
26	En-31	530	-466
27	En-355	520	-655
28	En-14	560	-525
29	En-21	570	-320
30	En-111	600	-360
31	En-325	620	-237
32	En-352	600	-384
33	En-353	560	-500
34	En-20	600	-461
35	En-20	500	-891

# (b) Bainitic steels.

No.	Steels	$B_S$ °C	$G_{max}$ J mol <sup>-1</sup>
1	En-28	440	-946
2	En-28	470	-818
3	En-30A	420	-979
4	En-30B	420	-1007
5	En-40B	450	-1007
6	En-38B	500	-633
7	En-320	520	-644



Fig. 8.7: Classification of En-Steels [BISRA, 1956b], (a) Widmanstätten ferrite and (b) bainite, on the basis of stored energy (as discussed in section 8.7).

Widmanstätten ferrite will then form below the  $Ae_3$  temperature when

$$G_{max} > G_1 \tag{8.16}$$

$$G_{max} > G_N \tag{8.17}$$

However, since the driving force necessary for detectable amount of nucleation (i.e.  $G_N$ ) should always be greater than that necessary to sustain growth,  $G_N$  will always exceed  $G_1$  and condition of Eq. 8.16 become redundant. Bainite will form below the  $T_o$  temperature when

$$G_{max} > G_2 \tag{8.18}$$

and

$$G_{max} > G_N \tag{8.19}$$

However, in any steel where the Widmanstätten ferrite transformation precedes bainite formation, condition of Eq. 8.19 will probably be redundant. This is because  $G_{max}$  varies approximately linearly and monotonically with temperature, so that once Eq. 8.16, has been satisfied, the further lowering of temperature will not in general lead to violation of Eq. 8.19.

#### 8.6.3.2 Widmanstätten Ferrite Formation

In the study of phase transformations, it is useful to know whether in the steel concerned, the nucleation of Widmanstätten ferrite is possible or not. By using the  $G_N$  curve it becomes possible to predict the  $W_S$  temperature in any particular steel.

Fig. 8.8 illustrates the two cases, the free energy  $G_{max}$  is plotted for a particular steel along with the  $G_N$  curve superimposed on it. As just discussed,  $G_N$  is the minimum amount of free energy required for the detectable nucleation of Widmanstätten ferrite irrespective of the chemical composition or carbon concentration of any particular steel. This implies that if the  $G_N$  curve lies above  $G_{max}$  curve than the nucleation of Widmanstätten ferrite is possible in that particular steel at any temperature (Fig. 8.8a). If the  $G_N$  curve lies below then there is not enough driving force for the nucleation of Widmanstätten ferrite. This situation is shown schematically in Fig. 8.8b, and the nucleation of Widmanstätten ferrite is not possible in between A and B, because there is not enough driving force available for the nucleation.

We have seen in Fig. 8.6 that the maximum free energy term *i.e.*,  $G_{max}$  is over a large temperature range linearly proportional to the temperature and this is also justified from the theory of isothermal martensitic nucleation. A detectable nucleation rate should only be possible in any particular steel if the free energy  $G_{max}$  for that steel exceeds  $G_N$  at the temperature concerned. Therefore,  $G_N$  curve of Fig. 8.6 will be assumed to be a universal curve expressing  $G_N$  as a function of temperature. This seems justified in view of the nature of the analysis and the wide range of steels accounted for in the calculation.

#### 8.7 Widmanstätten Ferrite Nucleation Kinetics

The results obtained in the preceding sections can be rationalised if it is assumed that the nucleation of Widmanstätten ferrite is similar to that of martensite, *i.e.*, the activation energy  $\Delta G^*$  for nucleation varies directly with the magnitude of the chemical driving force  $\Delta G$ , rather than the inverse square relationship implied by classical nucleation theory where  $G^* \propto (\Delta G)^{-2}$ . In martensite nucleation theory [Magee, 1970], this dependence is interpreted to imply the pre-existence of embryos, which simply need to grow rapidly to give what is in effect operational nucleation, controlled by the mobility of the embryo/matrix interface [Raghavan and Cohen, 1971, Olson and Cohen, 1976]. It is the activation energy for interface motion which is detected experimentally as that for nucleation. The analysis of kinetic data in sections 8.4-8.6, for a large number of steels indicated that due to the lower driving force available at the higher temperatures where Widmanstätten ferrite forms, it is necessary for its nucleation to occur by a paraequilibrium mechanism involving the partitioning of carbon, whereas that of martensite is diffusionless.

The implication of all this is that it becomes more difficult (*i.e.*, requires a larger driving force) to obtain a detectable degree of nucleation as transformation is suppressed to lower temperatures by solute additions, so that the  $W_S$  temperature decreases more rapidly than the  $Ae_3$  temperature with change in alloy chemistry. Further more, the free energy  $G_N$  necessary to obtain a detectable degree of transformation approximately a linear function of temperature:

$$G_N = A + B(T - 273.18) \tag{8.20}$$

and this is a universal function which can be applied to any low-alloy steel. The values of the constants A and B obtained by multiple regression analysis are given in Table 8.3.



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Temperature

(a)



(b)

Fig. 8.8: Schematic illustration of the significance of  $G_N$  curve in determining a detectable nucleation rate of Widmanstätten ferrite. (a) Nucleation is possible at any temperature. (b) Nucleation is not possible at temperatures between A and B.



Fig. 8.9: Schematic illustration of the conditions determining the Widmanstättenstart temperature  $(W_S)$ . The intersections at A and B determine the temperatures where the growth and nucleation conditions are satisfied. In the example illustrated, it is the growth which limits the  $W_S$  temperature.

The driving force  $G_{max}$  that is available for nucleation in any given steel, has to exceed  $G_N$ , giving the condition

$$G_{max} \le G_N. \tag{8.21}$$

where  $G_{max}$  as usual represents the maximum free energy change possible during nucleation, assuming that the nucleus adopts the chemical composition consistent with the maximum change in free energy, Fig. 8.5. The second condition that also has to be satisfied is that growth should be thermodynamically possible, so that the free energy change for growth (Fig. 8.4) should exceed the stored energy of Widmanstätten ferrite.

$$\Delta G^{\gamma \to \gamma' + \alpha} < -50 \text{ Jmol}^{-1} \tag{8.22}$$

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It is the simultaneous satisfaction of these two conditions which gives the highest temperature at which a detectable degree of reaction occurs. These concepts are illustrated schematically in Fig. 8.9.

#### 8.8 Analysis of Experimental Data on Widmanstätten Ferrite

The results obtained from the analysis of sections 8.4-8.6, are first applied to the experimental data of the present study and then in the following section to the data found in the published literature.

#### 8.8.1 Nucleation of Widmanstätten Ferrite in Alloys A3 and W1

The calculated driving force versus temperature curves are shown in Fig. 8.10, for both alloys. It is evident from Fig. 8.10, that the  $G_N$  curve lies above the free energy-temperature curves ( $G_{max}$ ) of all the alloys and the case is similar to the situation illustrated in Fig. 8.8a. It means that the nucleation of Widmanstätten ferrite over the whole range of temperature, is in principle possible in these alloys. Consistent with this, Fig. 8.11, shows a series of micrographs illustrating the formation of Widmanstätten ferrite in both alloys.

Table 8.3: The values of the constants A and B in equation 8.20.

Constants	Values
A	$-2489 \text{ J mol}^{-1}$
В	$3.531 \ { m J} \ { m mol}^{-1} \ {}^o{ m C}$



Fig. 8.10: Prediction of a detectable nucleation rate possible in (a) A3 and (b) W1 alloys, in these alloys the nucleation of Widmanstätten ferrite is possible at any temperature but Widmanstätten ferrite can only form at the temperature where enough driving force will be available for the growth.



(a)

(b)

Fig. 8.11: Formation of Widmanstätten ferrite in alloy A3 and W1 after austenitisation at 1100 °C for 10 min. (a) Alloy A3, isothermally transformed at 740 °C for 200 s showing blocky ferrite along with Widmanstätten ferrite plates at the austenite boundaries. (b) Weld deposit W1, ferrite allotriomorphs and Widmanstätten ferrite, the specimen having been transformed for 100 s at 670 °C.

#### 8.8.2 Nucleation of Widmanstätten Ferrite in Alloys A1 And A2

The driving force versus temperature curves are shown in Fig. 8.12, for these alloys. By inspection of Fig. 8.12, this situation is very similar to that of Fig. 8.8b, it is obvious that there is insufficient driving force for the nucleation of Wid-manstätten ferrite in the temperature range 420 to 680 °C. However, there is enough driving force available in the temperature range beyond 680 °C and below 420 °C. Nucleation of Widmanstätten ferrite in those regions should therefore be possible.

The formation of Widmanstätten ferrite in alloys A1 and A2 is shown in Fig. 8.13. In alloy A2 formation of Widmanstätten ferrite was observed at 700 °C, while the predicted lower limit was 680 °C. However, in alloy A1 Widmanstätten ferrite also formed below 675 °C, *i.e.*, in the region where there is apparently insufficient free energy available for the Widmanstätten ferrite nucleation. A close inspection of the microstructure (Fig. 8.13) revealed that a lot of carbide particles has precipitated within the allotriomorphic ferrite, matrix and Widmanstätten ferrite plates. Since carbide precipitation removes carbon from the system during transformation, it causes an increase in the free energy available for nucleation of Widmanstätten ferrite at lower temperatures. This might shift the  $G_{max}$  curve further below the  $G_N$  curve, making nucleation feasible. The other factor to be considered here is that if we consider the scatter in the data presented for the  $G_N$  curve in Fig. 8.6, the difference between calculated and experimentally determined temperature range can easily be reconciled. Hence, the nucleation of Widmanstätten ferrite in alloy A1 at this temperature is approximately consistent with the calculated data. The formation of Widmanstätten ferrite below the 420 °C is possible but due to the higher available driving force at such a low temperature, the bainite transformation takes precedence and replaces the formation of Widmanstätten ferrite.



Fig. 8.12: Prediction of the temperature range over which Widmanstätten ferrite can form at a detectable rate in alloys (a) A1 and (b) A2.



(b)

(a)

Fig. 8.13: Optical micrographs showing Widmanstätten ferrite formation in alloys A1 and A2. Both alloys were austenitised at 1100 °C for 10 min. (a) Alloy A1 after 12 days at 675 °C. b) Alloy A2 after isothermal transformation at 700 °C for 100 hr.

#### 8.9 Analysis of Published Experimental Data on Widmanstätten Ferrite

The recently published data [Aaronson *et al.* 1986] on the Widmanstätten-start temperature as a function of alloy chemistry, were analysed theoretically. Aaronson *et al.* were originally interpreted the data by considering the transition from allotriomorphic to plate-like ferrite to be determined by changes in the relative proportions of "partially coherent" and "disordered" regions of interface surrounding the ferrite particles. Whatever the details of the model [Aaronson *et al.* 1986], that theory is indeterminate since the proportion was found not to be constant, and could not be predicted as a function of alloy chemistry.

The calculations for majority of the steels studied by Aaronson *et al.* [1986] are presented in Figs. 8.15-8.16. A few of the steels they studied contained substantial amounts of copper, cobalt or aluminium, elements for which thermodynamic data compatible with the Lacher Fowler Guggenheim quasichemical solution model [Fowler and Guggenheim, 1939] used here, are not available. Consequently, those steels are not included in the analysis. Fig. 8.15 confirms that for almost all the steels listed in Table 8.4,  $W_S$  temperature is determined by equation 8.20, although for steel-11, which is heavily alloyed with Mn, the  $W_S$  temperature is suppressed to a greater extent, when compared with the  $Ae_3$  temperature, as is predicted by the present analysis. It is evident (Fig. 8.15) that there is very good agreement between experiment and theory.

Fig. 8.16 is plot between experimentally determined  $W_S$  and  $Ae_3$  temperature, shows that the  $W_S$  temperature is much more sensitive to the alloy composition than that of  $Ae_3$  temperature, which lead to the conclusion that in designing new highstrength weld deposits, alloy chemistry plays an important role in determining the extent of the Widmanstätten ferrite reaction.

Steel °C			Cher	nical (	Compo	sition	(wt.%	)		Temp	erature	е
No.	С	Si	Mn	$\operatorname{Cr}$	Mo	Ni	Al	Co	Cu	$W_{S(e)}$	$W_{S(c)}$	$Ae_3$
1	0.110	_	_	_	_	_	_	_		825	820	857
2	0.096	0.51	-	-	-		-	_	_	855	840	897
3	0.120	1.47	-	_	-	_	-	_	-	905	860	957
4	0.089	—	-	-	_	_	-	1.02	-	835		872
5	0.140	-	-	-	_		-	3.20	_	855	_	872
6	0.098	-	_	-	-	-	0.52	-	_	875	_	932
7	0.270	-	-	_	-	-	1.40	_	-	905	_	957
8	0.096	_	_	_	_		-	_	1.02	815	_	842
9	0.120	-	_	-	-	-	-	3.20	2.98	755	_	807
10	0.110	-	1.01	-	-	-	-			765	780	822
11	0.120	_	3.08	-	-	-	-	-	-	577	680	765
12	0.093	_	_	_	-	1.06	-	-	-	780	780	832
13	0.110	_	_	_	_	3.28	_	-	_	705	700	775
14	0.092	_	_	0.94		_	-	-	-	835	820	847
15	0.092	-	-	2.64	_	_		-	-	805	800	827
16	0.110	· ·	-	_	0.90	_	_	_	-	845	840	876
17	0.110	-	_		1.95	_	_	-	-	855	860	902

Table 8.4: Chemical compositions of the steels used by Aaronson et al. [1986].

Values of  $W_{S(c)}$  are from present work and those of  $W_{S(e)}$  are due to Aaronson *et al.* [1986].


Fig. 8.15: Comparison of the calculated and experimentally determined [Aaronson et al. 1986] Widmanstätten ferrite-start  $(W_S)$  temperatures.



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Fig. 8.16: Plot of experimental  $(W_S)$  and  $Ae_3$  temperatures for the steels studied by Aaronson et al. [1986]. The plot shows that the  $(W_S)$  temperature is much more sensitive of the alloy chemistry than  $Ae_3$  temperature.

# 8.10 Conclusions

the problem of nucleation of Widmanstätten ferrite has studied in detail, both theoretically and experimentally. It is concluded that the nucleation of Widmanstätten ferrite can be best studied if it assumed that it follows the same mechanism as that for isothermal nucleation of martensite of preexisting embryos, but with the diffusion of carbon during nucleation. In this mechanism the free energy change for nucleation is directly proportional to the temperature rather than  $\Delta G^* \propto (\Delta G)^{-2}$  type relation expected by the classical nucleation theory.

The results of thermodynamic analysis have been applied to new experimental data and those data found in the published literature. It was found that the data can be predicted to a fair accuracy.

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# Chapter 9 THE GROWTH OF WIDMANSTÄTTEN FERRITE PLATES AND BAINITE SHEAVES

# 9.1 General Introduction

The final mechanical properties of a weld deposit or a wrought steel depend on a number of variables such as chemical composition, cooling conditions and the process itself, final microstructure. In addition the presence of various transformation products, determines the final microstructure of the weld deposit or the steel, and hence the mechanical properties. For example, it is known that the presence of Widmanstätten ferrite leads to poor toughness [Savage and Aaronson, 1966, Rodrigues and Rogerson, 1977] because of its larger effective grain size and preferred orientation which offers a little resistance to the crack propagation. Bainitic steels, however, show a remarkable combination of toughness and strength [Nakasugi *et al.* 1983] and acicular ferrite is the most desirable phase [Grong and Matlock, 1986] from the toughness point of view. The presence of both Widmanstätten ferrite and bainite directly affect the mechanical properties, and therefore, knowledge about their growth is of commercial as well as academic interest.

# 9.1.1 Growth of Widmanstätten Ferrite and Bainite

A critical assessment of the diffusion-controlled growth of ferrite plates in plain carbon steels indicates that in these steels, plates of Widmanstätten ferrite lengthen at a rate which is approximately consistent with growth controlled by the diffusion of carbon in the austenite ahead of the transformation interface [Bhadeshia, 1985]. The growth of bainite sheaves was on the other hand, found to occur at a rate much faster than expected from carbon diffusion-controlled transformation. These conclusions are consistent with current models for transformations in steels, which assume that Widmanstätten ferrite grows by a displacive para-equilibrium transformation mechanism whereas bainite grows by displacive transformation in the form of sheaves of platelets called subunits. Each subunit inherits the composition of the parent phase and any excess carbon is subsequently partitioned into the residual austenite or precipitated in the form of carbides within the bainitic ferrite [Bhadeshia and Waugh, 1982].

In early work on Fe-Ni-C alloys containing relatively high concentrations of nickel, the experimentally measured lengthening rates of bainite were found to be very much *lower* than expected from carbon diffusion-controlled growth [Goodenow

et al. 1963; Rao and Winchell, 1967]. Consequently it has been suggested that relatively large concentrations of nickel may, via some kind of an interface/solute interaction, retard growth kinetics [Rao and Winchell, 1967, Purdy and Hillert, 1984]. However, since the original work [Goodenow et al. 1963, Rao and Winchell, 1967] was published, there have been many refinements to the theory and other aspects concerning the diffusion-controlled growth of plates [Bhadeshia, 1985]. Consequently, the purpose of this work was to reassess the experimental data on bainite growth kinetics in nickel-rich steels in particular, and any other relevant data on alloy steels in general. The early experiments were all based on measurements carried out using light microscopy, a technique which has limited resolution as far as the structure within sheaves of bainite is concerned. They are consequently assumed to refer to the growth rate of sheaves of bainite, rather than to the subunits within the sheaves.

The following chapter is devoted to an attempt at understanding the growth mechanism and the growth rate of Widmanstätten ferrite and bainite. Initially a brief description of the current mechanisms of understanding the formation of both phases is given, the theory of carbon diffusion-controlled growth is then described, and finally, published experimental data on the lengthening rate of sheaves of bainite in alloy steels are analysed and compared with theory.

## 9.2 Widmanstätten Ferrite

As already stated, Widmanstätten ferrite is an undesirable constituent of a (weld) microstructure because its presence can sometimes lead to poor toughness in low-alloy steels [Savage and Aaronson, 1966, Nakasugi *et al.* 1983]. Widmanstätten ferrite forms as long plates nucleating from previously formed allotriomorphic ferrite layers and growing inwards within the austenite grain structure. Fig. 9.1 shows a typical Widmanstätten ferrite microstructure observed in a Fe-0.4C-2.0Si wt. % alloy. The main characteristic of Widmanstätten ferrite is its long plate-like morphology and the tendency to form in packets of identically orientated plates, thus offering little resistance to cleavage crack propagation.

The formation of Widmanstätten ferrite is also accompanied by a change in the shape of the transformed region. The shape change due to a single wedge of Widmanstätten ferrite has been found to consist of two adjacent and opposing invariant-plane strain (IPS) deformations [Bhadeshia, 1981].



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Fig. 9.1: Optical micrograph showing the Widmanstätten ferrite microstructure in Fe-0.4C-2.0Si wt. % steel, specimen austenitised at 1300 °C for 10 min and then isothermally transformed at 680 °C for 5 min. Note the long plates of Widmanstätten ferrite evolved from the grain boundary allotriomorphic ferrite layer, and their parallel formation.

These IPS deformations each have a large shear component [Watson and Mc-Dougall, 1973] and imply the existence of an atomic correspondence between the parent and product phases as far as the iron and substitutional solute atoms are concerned. Interstitial atoms, such as, carbon can diffuse during growth without affecting the shape change or the displacive nature of the transformation. The cooperative growth of a pair of adjacent mutually-accommodating crystallographic variants allows the elastically accommodated strain energy accompanying plate for-

mation to be rather small, of the order of 50 J mol<sup>-1</sup> [Bhadeshia, 1981]. This is consistent with the temperatures at which Widmanstätten ferrite forms and the wedge morphology which arises because the adjacent variants have slightly different habit planes. The shape change indicates that the  $\alpha / \gamma$  interface is glissile and the plates can therefore grow at a constant rate controlled by the diffusion of carbon in the austenite ahead of the plate tip. Widmanstätten ferrite cannot be put in the group of diffusional transformation products, because there is no diffusion involved in the actual lattice change; iron and substitutional elements do not diffuse during transformation. There is no reconstructive diffusion [Bhadeshia, 1981] during the formation of Widmanstätten ferrite.

### 9.3 Bainite

Bainite is a non-lamellar mixture of ferrite and carbides and forms in the temperature range where diffusional transformation gives way to displacive growth. Bainite consists of aggregates of ferrite platelets and residual phases such as martensite, the ferrite being in the form of clusters of thin platelets, commonly called subunits, and the cluster individually being referred to as sheaves of bainite [Aaronson and Wells, 1956].

Sheaves of bainite normally nucleate at austenite grain boundaries (Fig. 9.2) and propagate towards the grain interiors by the "nucleation" and growth of individual subunits [Oblak and Hehemann, 1967]. New subunits nucleate near the tips of previous subunits as shown in Fig. 9.4; the nucleation of subunits in adjacent positions occurs at a much lower rate. This means that the sheaf itself has, on a macroscopic scale, a plate-like morphology in three dimensions. Since coordinated movements of atoms cannot in general be sustained across austenite grain boundaries, and so the growth of a given sheaf is confined strictly to a single austenite grain.

Bainite probably forms by a diffusionless displacive transformation mechanism. The formation of bainite is also accompanied by a change in the transformed region if a polished specimen is allowed to transform to bainite as shown in Fig. 9.4. This shape change is similar to that shown by martensite and Widmanstätten ferrite *i.e.*, an invariant-plane strain (IPS) type.

#### 9.4 Theory of Carbon Diffusion-Controlled Growth

Particle dimensions during diffusion-controlled growth vary parabolically with time when the extent of the diffusion field in the matrix increases with particle size.



Fig. 9.2: Optical micrograph showing a bainitic microstructure in a Fe-0.22C-2.05Si-3.07Mn-0.7Mo wt.% alloy. Specimen austenitised at 900 °C for 5 min and then isothermally transformed for bainite at 400 °C for 1000 s.



Fig. 9.3: TEM micrograph showing the sub-unit structure of bainite sheaves in a Fe-0.22C-2.05Si-3.07Mn-0.7Mo wt.% alloy. Specimen austenitised at 900 °C for 5 min and then isothermally transformed for bainite at 400 °C for 1000 s.



Fig. 9.4: Surface relief accompanied by the formation of bainite in Fe-0.22C-2.05Si-3.07Mn-0.7Mo wt.% steel. Surface upheavals were imaged by using Nomarski prism. Specimen austenitised at 900 °C for 10 min and then isothermally transformed to bainite at 400 °C for 1000 s.

The growth rate thus decreases with time. On the other hand, Widmanstätten ferrite plates are found experimentally to grow with a constant velocity. It has been demonstrated that Widmanstätten ferrite plates form with equilibrium or paraequilibrium carbon concentration and that the partition of carbon during the growth process is a thermodynamic necessity [Bhadeshia, 1981]. The distribution of carbon during the growth of Widmanstätten ferrite is shown schematically in Fig. 9.5.



Fig. 9.5: Schematic representation of the distribution of carbon during the formation of Widmanstätten ferrite plates.

The diffusion-controlled lengthening of plates or needles can, however occur at a constant rate because solute can be partitioned to the sides of the plates. The shape change accompanying Widmanstätten ferrite growth implies the existence of a glissile  $\alpha / \gamma$  interface and since carbon is partitioned during growth, the rate of growth can be expected to be controlled by the diffusion of carbon in the austenite ahead of the moving interface, even when the reaction occurs at a low homologous temperature. As already stated, iron and substitutional atoms do not diffuse during the growth of Widmanstätten ferrite and bainite and there is no reconstructive diffusion during transformation.

# 9.5 Theoretical Analysis

Of the various kinetic models available so far, [Zener, 1946; Hillert, 1957; Horvay and Cahn, 1961; Trivedi, 1970] the model proposed by Trivedi [1970] is the most recent one which assesses the relative contributions of diffusion, surface energy and interface kinetic processes during the growth of plate shaped precipitates.

Trivedi [1970] has obtained a solution for the diffusion-controlled growth of parabolic cylinders (an approximation to a plate morphology). The steady state growth velocity v, controlled by the diffusion of carbon in the austenite ( $\gamma$ ) ahead of the interface, is obtained by solving the equation:

$$f_1 = (\pi p)^{\frac{1}{2}} exp\{p\} erfc\{p^{\frac{1}{2}}\} [1 + \frac{r_c f_1 S_2\{p\}}{r}]$$
(9.1)

where

$$f_1 = \frac{\overline{x} - x^{\gamma \alpha}}{x^{\alpha \gamma} - x^{\gamma \alpha}}$$

In this equation,  $\overline{x}$  is the undisturbed carbon concentration in the austenite, well ahead of the plate tip, and can be taken to be equal to the average carbon concentration in the alloy if soft impingement effects are absent.  $x^{\gamma\alpha}$  and  $x^{\alpha\gamma}$  are the paraequilibrium carbon concentrations in the austenite and ferrite respectively. pis the Péclet number, a dimensionless velocity given by

$$p = \frac{vr}{2\overline{D}} \tag{9.2}$$

where v is the diffusion-controlled growth velocity. The function  $S_2$  has been evaluated numerically by Trivedi [1970]. The diffusion coefficient  $D\{x, T\}$  depends on the carbon concentration x, which in turn is a function of the distance ahead of the plate tip, therefore, the diffusivity used in Eq. 9.2 is a weighted average [Trivedi and Pound, 1967]:

$$\overline{D} = \int_{x_r}^{\overline{x}} \frac{D\{x, T\}}{\overline{x} - x_r} dx$$
(9.3)

where  $x_r$  is the carbon concentration in the austenite at the plate tip, and D is evaluated using the Siller and McLellan model [Bhadeshia, 1982a; Siller and McLellan, 1969; 1970] for the diffusion of carbon in austenite.  $x_r$  differs from the paraequilibrium concentration because of the curvature of the interface at the plate tip. It can be calculated using the following equation [Christian, 1975]:

$$x_r = x^{\gamma \alpha} [1 + \frac{\Gamma}{r}] \tag{9.4}$$

where

$$\Gamma = \frac{\sigma V_m (1 - x^{\gamma \alpha}) / (x^{\alpha \gamma} - x^{\gamma \alpha})}{RT [1 + \frac{d(\ln\{a\})}{d(\ln\{x^{\gamma \alpha}\})}]}$$

 $\sigma$  is the interface free energy per unit area, taken to be 0.2 Jm<sup>-2</sup> [Bhadeshia, 1985], *a* is the activity coefficient for carbon in austenite, *R* is the universal gas

constant, T is the absolute temperature of transformation and  $V_m$  is the molar volume of ferrite [Bhadeshia, 1985]. The paraequilibrium carbon concentration in the austenite (i.e.,  $x^{\gamma\alpha}$ ) and the activity coefficient a were calculated using the Lacher-Fowler-Guggenheim quasichemical thermodynamic model [Shiflet *et al.* 1978] and the thermodynamic data given in detail in [Bhadeshia, 1985]. The free energy data for pure iron were obtained from Kaufman *et al.* [1963]. This is believed to make the analysis more reliable for extrapolation to low temperatures [Bhadeshia, 1985]. The paraequilibrium carbon concentration  $x^{\alpha\gamma}$  is always so small, that it was estimated using the values for plain carbon steels deduced by Bhadeshia [1982b].

#### **9.5.1** Extrapolation of the Phase Boundaries

Both Widmanstätten ferrite and bainite form below the eutectoid temperature and because experimental data for  $x^{\alpha\gamma}$  and  $x^{\gamma\alpha}$  are not available, therefore  $\alpha / (\alpha + \gamma)$  and  $\gamma / (\alpha + \gamma)$  phase boundaries have to be extrapolated. Finally, because both Widmanstätten ferrite and bainite grow by a displacive transformation mechanism [Bhadeshia and Waugh, 1982], the calculations must take account of the strain energy resulting from the invariant-plane strain shape change accompanying their formation. The stored energy terms for Widmanstätten ferrite and bainite are about 50 and 400 J mol<sup>-1</sup> respectively [Bhadeshia and Waugh, 1982], and are taken into account according to Bhadeshia [1985]. For illustration purposes, the calculations have been carried out using three different stored energy values of 0, 50 and 400 J mol<sup>-1</sup>, although only the last set of calculations is strictly relevant for the present work, which deals with bainite.

### 9.5.2 Materials

The chemical compositions of the steels [Hillert, 1960; Goodenow *et al.* 1963; Rao and Winchell, 1967; Oblak and Hehemann, 1967; Speich and Cohen, 1960; Nemoto, 1974; and Simonen et 1973] studied are listed in Table 9.1. The thermodynamic calculations take account of all the elements listed, and an effect on the diffusion coefficient of carbon in austenite is included through their influence on the activity of carbon in austenite [Bhadeshia, 1982a]. Note that some of the steels are not substitutionally alloyed, but were missed in the earlier assessment on Widmanstätten ferrite plates growth [Bhadeshia, 1985] and have been included in the analysis for completeness.

Steel	Chemical Composition (wt. %)				Reference			
No.	С	Si	Mn	Ni	Mo	Cr		
1	0.25	-	-	1.00	0.0	0.0	Hillert, 1960	
2	0.29	0.0	0.0	-	-	-	-ditto-	
3	0.36	1.00	-	-	-	-	-ditto-	
4	0.46	1.00	-	-	-	-	-ditto-	
5	0.49	-	_	-	-	-	-ditto-	
6	0.53	-	-	1.00	-	-	-ditto-	
7	0.55	1.00	-	-	-	-	-ditto-	
8	0.21	0.02	0.26	-	-	-	-ditto-	
9	0.35	0.28	0.58	-	-	-	-ditto-	
10	0.42	0.08	0.28	_	-	-	-ditto-	
11	0.59	0.25	0.56	-	-	-	-ditto-	
12	0.81	0.26	0.23	-	-	-	-ditto-	
13	0.10	0.18	0.79	8.70	0.07	0.21	Goodenow et al. 1963	
14	0.50	0.36	0.68	8.70	-		-ditto-	
15	0.19	0.29	0.60	8.90	-	-	-ditto-	
16	0.29	0.31	0.69	8.80	-	-	-ditto-	
17	0.026	-	-	10.6	-	-	Rao and Winchell, 1956	
18	0.043	-	-	10.6	-	-	-ditto-	
19	0.058	-	-	10.6	-	-	-ditto-	
20	0.086	-	-	10.6	-	-	-ditto-	
21	0.162	-	-	10.6	-	-	-ditto-	
22	0.69	0.70	0.85	1.80	0.81	0.85	Oblak and Hehemann, 1967	
23	0.50	0.36	0.68	8.70	-	-	-ditto-	
24	0.96	-	_	-	-	-	Speich and Cohen, 1960	
25	1.16	-	-	-	-	-	-ditto-	
26	1.43	-	-	-	-	-	-ditto-	
27	1.14	-	-	-		2.70	-ditto-	
28	1.12	-	-	5.28	-	-	-ditto-	
29	0.51	-	-	9.10	-	-	Nemoto, 1974	
30	0.24	0.003	0.002	-	-	-	Simonen et al. 1973	
31	0.33	0.002	0.002	_	-	_	-ditto-	

Table 9.1: Chemical compositions in wt. %.

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#### 9.6 Results and Discussion

The calculated  $\gamma/(\alpha + \gamma)$  phase boundaries, representing the variation in  $x^{\gamma\alpha}$  as a function of temperature and stored energy, are presented in Fig. 9.6.

#### 9.6.1 Growth of Widmanstätten Ferrite

The growth rate of Widmanstätten ferrite plates has been considered in detail by Bhadeshia [1981], and therefore the work presented here is limited to only those data which were missed in the original analysis. The results are presented in Figs. 9.7 and 9.8. Consistent with the original analysis, the measured growth rates are higher (generally an order of magnitude) than those calculated by the carbon-diffusion controlled growth theory, even though the calculations are based on the assumption of the Zener maximum-velocity hypothesis.

#### 9.6.2 Growth of Bainite Sheaves

The growth rate calculations of bainite sheaves are presented in Figs. 9.9-9.13, for all the steels listed in Table 9.1, with the exception of steels 24-29. For steels 24-28, the transformation to bainite was carried out under conditions where the diffusivity of carbon in austenite had to be calculated for exceptionally high values of  $x^{\gamma\alpha}$ . The Siller and McLellan theory for the diffusion coefficient of carbon [Bhadeshia, 1982a; Siller and McLellan, 1969], although known to be highly reliable in both the thermodynamic and kinetic sense, is unable to cope with carbon concentrations in excess of about  $\frac{1}{7}$  mole fraction. Consequently, growth calculations could not be carried out for steels 24-28. For steel 29, only one experimental growth rate of  $5 \times 10^{-8}$  m s<sup>-1</sup> was reported, for a transformation temperature of  $380 \ ^{\circ}$ C; the calculated growth rates for stored energy values of 0, 50 and 400 J mol<sup>-1</sup> are found to be  $5.178 \times 10^{-8}$ ,  $4.255 \times 10^{-8}$  and  $6.874 \times 10^{-9}$  m s<sup>-1</sup> respectively.

For steels 30 and 31, some of the experimental data are found to be slower than calculated. This may be because these are low hardenability steels and therefore some transformation could took place during cooling, which interfere the bainite reaction.



Fig. 9.6: Continued.....



Fig. 9.6: Effect of stored energy upon carbon content of austenite for the steels in Table 9.1.



Fig. 9.7: Continued.....



Fig. 9.7: Calculated and experimental growth rates of Widmanstätten ferrite plates. Experimental data due to Hillert, [1960] and growth rates calculated using carbon diffusion controlled growth rate theory assuming a plate morphology of Widmanstätten ferrite and taking into account a stored energy of 50 J mol<sup>-1</sup>.



Fig. 9.8: Combined graph of calculated and experimental growth rates of Widmanstätten ferrite plates. Experimental data due to Hillert, [1960] and growth rates calculated using carbon diffusion-controlled growth rate theory assuming plate morphology of Widmanstätten ferrite and taking into account a stored energy of 50 J  $mol^{-1}$ .



Fig. 9.9: Comparison of experimental (curve 1) and calculated bainite growth rates. Curves 2-4 are calculated using stored energies of 0, 50, 400 J mol<sup>-1</sup> respectively. The experimental data are due to Goodenow et al. [1963].



Fig. 9.10: Comparison of experimental (curve 1) and calculated bainite growth rates. Curves 2-4 are calculated using stored energies of 0, 50, 400 J mol<sup>-1</sup> respectively. The experimental data are due to Rao and Winchell [1967].



Fig. 9.11: Comparison of experimental (curve 1) and calculated bainite growth rates. Curves 2-4 are calculated using stored energies of 0, 50, 400 J mol<sup>-1</sup> respectively. The experimental data are due to Oblak and Hehemann [1967] (Table 9.1 steel-22).



Fig. 9.12: Comparison of experimental (curve 1) and calculated bainite growth rates. Curves 2-4 are calculated using stored energies of 0, 50, 400 J mol<sup>-1</sup> respectively. The experimental data are due to Oblak and Hehemann [1967] (Table 9.1 steel-23)



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Fig. 9.13: Comparison of experimentally measured growth rate of bainite sheaves with the growth rates calculated by carbon diffusion-controlled growth theory.

It is evident from a comparison of the experimental data with the 4th curve on each figure, that the growth rate of bainite sheaves always exceeds that expected on the basis of carbon diffusion-controlled paraequilibrium transformation. This might intuitively be expected to be the case since there are now considerable data to indicate that bainite forms by diffusionless transformation, the excess carbon in the bainitic ferrite being partitioned or precipitated subsequent to transformation [Bhadeshia and Waugh, 1982, Christian and Edmonds, 1984]. However, the lengthening rate of a *sheaf* of bainite does not depend just on the rate of subunit lengthening, but also on the rate at which new subunits are nucleated. The overall lengthening rate of a sheaf may in fact be very low if the nucleation rate of subunits is sufficiently small, even though individual subunits may grow rapidly.

If it is assumed that a subunit reaches its limiting size in a time interval t, and

that the time  $\Delta t$  elapsed before another subunit nucleates at the tip of the original subunit, then the lengthening rate  $V_s$  of a sheaf is given by:

$$V_s = \frac{V}{1 + \frac{\Delta t}{t}} \tag{9.5}$$

where V is the average lengthening rate of a subunit. Because the growth of a subunit is diffusionless, V is expected to exceed the rate v calculated on the basis of carbon diffusion-controlled growth, although  $V_s$  will only be greater than v if the factor  $[1+(\Delta t/t)]$  is sufficiently small (i.e., if the time interval between the nucleation of subunits is small in comparison with the time required for the subunits to reach their limiting size). The results in general indicate that  $V_s >> v$  so that it can be safely concluded that the growth rate of the subunits is much faster than expected from carbon diffusion-controlled transformation. This is consistent with direct high-resolution observations on the growth of bainite subunits in an Fe-Mn-Si-C alloy [Bhadeshia, 1984]. The results also indicate that solute/interface interactions are not strong enough to slow down interface motion to velocities less than v, and that there is no special nickel-atom/interface interaction in Fe-Ni-C alloys, as has been suggested in the past [Rao and Winchell, 1967, Purdy and Hillert, 1984]. This conclusion also applies to Cr which is a significant alloying element in some of the steels analysed in the present.

#### 9.7 Conclusions

It has been found that the lengthening rates of sheaves of bainite in alloys steels are far greater than expected from calculations based on carbon diffusion-controlled paraequilibrium transformation. Furthermore, it is found that the lengthening rates of individual bainite subunits within the sheaves must also be faster than carbon diffusion-controlled growth. The results are consistent with the proposed mechanism of the bainite transformation in which the growth of the bainite subunits is diffusionless, with the partitioning of carbon into the residual austenite occurring immediately after transformation.

# Chapter 10 ON THE FORMATION OF INTRAGRANULAR WIDMANSTÄTTEN FERRITE PLATES IN ULTRA HIGH STRENGTH STEELS

# **10.1 Introduction**

A number of ferrite morphologies are observed in wrought steels and steel weld deposits, when austenite is allowed to transform isothermally below the  $Ae_3$  temperature depending upon for example, the austenitisation conditions, alloy chemistry, and cooling rates. These austenite decomposition products can be allotriomorphic ferrite, Widmanstätten ferrite, bainite or acicular ferrite. Widmanstätten ferrite usually grows either from prior austenite grain boundaries or from the already transformed grain boundary allotriomorphic ferrite and form in parallel formations *i.e.*, several plates nucleate and grow parallel to each other in packets. The final mechanical properties of the steel or weld deposits are closely related to the proportions of these phases in the microstructure.

Many observations have demonstrated that during cleavage failure, the cracks propagate virtually undeviated across individual sheaves of bainite in low-carbon, low-alloy steels [Pickering, 1967]. Similar results have been reported for low-carbon, low-alloy weld deposits, where qualitative evidence suggests that cleavage cracks propagate undeflected across packets of identically orientated bainite platelets but have to reinitiate on encountering sheaf boundaries [Chandel et al. 1985]. The size of cleavage facets obtained by brittle fracture is found to correlate well with the width of bainite sheaves, *i.e.*, the packet size [Naylor and Krahe, 1974], although there are other results which suggest that the unit crack path is somewhat larger than the packet size [Ohmori et al. 1974; Brozzo et al. 1977]. The unit crack path length is defined simply as the region within which the crack propagates in a nearly straight fashion [Matsuda et al. 1968, 1972]. The fact that the path length tends to be somewhat larger than the sheaf width, may have something to do with the fact that adjacent bainite sheaves, which are different variants of the orientation relationship with austenite may still have their cleavage planes fairly parallel [Brozzo et al. 1977]. Thus, any discrepancy between the packet size and unit crack path length does not weaken the basic argument that having a set of parallel ferrite plates in identical orientation is bad for toughness. Instead, it leads to a more general condition that groups of plates with a common cleavage plane should be avoided.

The idea that a "chaotic" microstructure (rather than one in which the ferrite plates are neatly arranged into packets) is better for toughness is very prominent in the welding industry [Savage and Aaronson, 1966; Rodrigues and Rogerson, 1977; Garland and Kirkwood, 1975; Billy et al. 1980]. Hence, controlled quantities of specific kinds of nonmetallic inclusions are tolerated in weld deposits, because they serve to stimulate the intragranular nucleation of ferrite platelets which radiate in many different directions from the inclusion nucleation sites; such a microstructure in welds is denoted " acicular ferrite", although it is now appreciated that acicular ferrite is nothing but intragranularly nucleated bainite [Bhadeshia, 1989]. A propagating crack then has to traverse plates in many different crystallographic orientations. Nonmetallic inclusions are otherwise regarded as harmful, since they can in many circumstances, be responsible for initiating cleavage or void nucleation. Using the same reasoning, deliberate additions of titanium oxide particles have recently been made to wrought steels in order to induce the intragranular nucleation of acicular ferrite [Yamamoto et al. 1987; Chijiiwa et al. 1988; Bhadeshia, 1989].

In quenched and tempered martensitic steels, fractographic measurements indicate that the dominant microstructural feature in the process of cleavage fracture is the size of the martensite packet [Roberts, 1970]. For heavily-alloyed ultra highstrength steels, ausformed martensites have been demonstrated to have a more chaotic spatial and size martensitic microstructures [Hornbogen, 1989]. This is one of the reasons why ausformed steels also have a higher level of strength without unduly sacrificing the toughness. Tomita and Okabayashi [1983, 1985] demonstrated improvements in the mechanical properties of martensitic steels, when the austenite grain structure was first partitioned into smaller regions by partial transformation to bainite. The small quantity of grain boundary nucleated bainite sheaves effectively refined the austenite grains prior to martensitic transformation.

The purpose of the work presented here was to investigate an alternative method of achieving the same effect, suggested by recent research on Fe-Cr-Mo-C weld deposits [Babu and Bhadeshia, 1990]. The intragranular nucleation can be stimulated if the austenite grain boundaries are removed as potential heterogeneous nucleation sites, by decorating them with thin layers of allotriomorphic ferrite (Fig. 10.1).

For the technique to work, the allotriomorphic ferrite must not act as a substrate for either secondary Widmanstätten ferrite or bainite, since both of these are in the form of undesirable packets of parallel platelets, and indeed, consume austenite which should be preserved for intragranularly nucleated transformation products. The allotriomorphic ferrite can be rendered innocuous if austenite stabilising elements partition during its growth. This method of stimulating intragranular nucleation is particularly relevant in the context of high-strength steels, because unlike weld deposits, they have to be cleaner in order to ensure adequate toughness, so that the number of oxide particles present can be very limited indeed. It is their high strength which makes them much more susceptible to nonmetallic inclusions as fracture initiators. The experiments reported here are consequently conducted on high purity steels, with the aim of producing a microstructure in which the packets of martensite are refined by the presence of intragranularly nucleated Widmanstätten ferrite.

## **10.2 Experimental Procedures**

Initially the material selected for this study were medium carbon high hardenability alloys. which were heavily alloyed with Si and Mn. These materials were purposely selected because of two reasons. Because they contain a high content of Mn which is austenite stabiliser thus can increased the incubation time for high temperature ferrite products and the silicon is a ferrite stabiliser. The high silicon content also made the carbide precipitation sluggish so that ferrite or bainite reaction can be studied without any interruption of the cementite precipitation. The chemical composition of material used are given in Table 10.1.

	С	Si	Mn	Mo	Al	Ti	0
A1	0.22	2.07	3.00	_	0.011	0.004	0.0035
A2	0.22	2.05	3.07	0.70	0.005	0.004	0.0057

Table 10.1: Chemical compositions (wt.%) of the alloys used in this investigation.

The alloys A1 and A2 were hot rolled round bars of 10 mm diameter in the as received condition. Throughout this investigation two types of specimens were used. One set had the form of 10 mm long rods of 3 mm diameter§ for isothermal heat treatments and optical study. The other samples were square sections with 10 mm edges, for surface relief experiments§.

<sup>§ 3</sup> mm diameter was selected to facilitate transmission electron microscopy at any stage of the experiments.

 $<sup>\</sup>S$  The specimen preparation methods have been described in Chapter 3.

Fig. 10.2 illustrates schematically the types of heat treatment cycles were used during the present study. Before any isothermal transformation austenitisation treatments generally performed at 1100 or 1300 °C for 15 min to produce larger austenite grains, while the specimens were sealed in quartz capsules under a partial pressure of pure argon. After austenitisation the samples were taken out from the furnace, the quartz capsule was carefully broken and then immediately quenched into a fluidized bed, which was maintained at the reaction temperature (controlled to  $\pm$  3 °C), reacted for different time durations and then finally quenched into iced-water. The heat-treatment schedules are given in Table 10.2.

For surface relief experiments, specimens were mechanically polished to a  $\frac{1}{4}$   $\mu$ m finish, and sealed in quartz capsules. The heat treatments were carried out in the same way as described in the previous section except that after austenitisation, the quartz capsules were not broken but simply transferred to the fluidized bed maintained at the reaction temperature, reacted for the predetermined time and then the capsule was quenched into ice cooled water.

Any surface relief effects were imaged using the Nomarski differential interference technique with a Ziess optical microscope. The tilt sense was determined by through focusing experiments, using grain boundary grooves for reference. Upward upheavals consisting of two adjacent and opposing invariant-plane strains referred to as "tent-like" compared with a similar net depression of the free surface which are referred to as "vee-shaped" surface relief effects.

Optical microscopy of the heat treated specimens were carried out using conventional metallography techniques. Optical specimens were etched in 2nital solution and were examined using an Olympus microscope, fitted with Olympus 35 mm camera.

Thin foil specimens were prepared from the heat treated samples for electron microscopy by the methods given in Chapter 3, and examined in a PHILIPS EM400T transmission electron microscope operated at 120 kV, equipped with a LINK 860 energy dispersive analysis system to facilitate microanalysis. Standard thin foil correction programmes were used to compensate for X-ray detection efficiency and absorption. For quantitative analysis the specimen was tilted to 35° towards the detector. Since this reduced the astigmatism in the image and improved the working resolution.

# **10.3 Theoretical Analysis of Transformation Characteristics**

It is found that Widmanstätten ferrite can nucleate at a detectable rate when

[Bhadeshia, 1981]

$$G_{max} \le G_N. \tag{10.1}$$

 $G_{max}$  represents the free energy change during nucleation, assuming that the nucleus adopts a composition which maximises this change.  $G_N$  is a nucleation function (linear with temperature and common to all steels) representing the free energy change which has to be exceeded before Widmanstätten ferrite can form at a detectable rate. In addition to this condition, growth should also be thermodynamically possible, so that the free energy change for growth  $(\Delta G^{\gamma \to \gamma + \alpha})$  should exceed the stored energy of Widmanstätten ferrite

$$\Delta G^{\gamma \to \gamma' + \alpha} < -50 \text{ J mol}^{-1}. \tag{10.2}$$

Since the nucleation of bainite and Widmanstätten ferrite is described by the same function  $G_N$ , the nucleus is assumed to develop into bainite if the driving force for growth is sufficient to permit its diffusionless growth. Thus, bainite and Widmanstätten ferrite are normally represented by the same C-curve on the time-temperature-transformation (TTT) diagram, with Widmanstätten ferrite forming between the  $W_S$  and  $B_S$  (Widmanstätten ferrite-start and bainite-start respectively) temperatures and bainite forming below  $B_S$ . These concepts have already been illustrated schematically in Fig. 7.10.

The aim was to induce the intragranular nucleation of a small volume fraction of Widmanstätten ferrite plates, in such a way that the plates do not grow in parallel formations. Nucleation on inclusions can achieve this because their sub-micron size cannot in general support the formation of more than one plate (although autocatalysis [Olson and Cohen, 1986] can stimulate the formation of other plates in close proximity). Particle nucleation is unlikely to have an opportunity to occur if the austenite grain boundary nucleation sites are active, since they are known [Ricks *et al.* 1982] to be more effective nucleants, so that transformation originating from the grain surfaces can swamp any intragranular events. Grain boundary nucleated (*i.e.*, secondary) Widmanstätten ferrite also has the unfortunate tendency to grow in packets of parallel plates. The boundaries can be rendered ineffective by decorating them with uniform, thin layers of allotriomorphic ferrite [Babu and

<sup>§</sup> The TTT diagram can be considered to consist of two 'C' curves, the one at higher temperatures representing reconstructive transformations such as allotriomorphic ferrite and pearlite, and the other, extending to lower temperatures, for displacive reactions such as Widmanstätten ferrite and bainite [Bhadeshia, 1981].

Bhadeshia, 1990] which, due to the partitioning of austenite stabilising elements into the surrounding matrix, can be prevented from acting as substrates for the growth of secondary Widmanstätten ferrite. The steel utilised must therefore be very sluggish in its transformation to allotriomorphic ferrite.

High-strength steels are in this respect eminently suitable, because they are usually heavily alloyed for the sake of hardenability. A less well known effect first predicted theoretically is that the alloying leads to a splitting of the displacive C-curve of the TTT diagram into separate Widmanstätten ferrite and bainite curves [Bhadeshia and Svensson, 1989]. The  $G_{max}$  function is significantly curved at high temperatures, so that it can in principle intersect the  $G_N$  line at two points (Fig. 10.3). Widmanstätten ferrite ferrite can then form at elevated temperatures above the upper intersection temperature, and bainite at temperatures below the lower intersection (assuming that its growth is thermodynamically possible).

The steels used in the present study exhibit precisely this kind of behaviour, as illustrated in the calculated diagrams presented in Fig. 10.4. The heat-treatments were designed to take advantage of the form of the TTT diagram, which indicates that allotriomorphic ferrite forms long before the onset of Widmanstätten ferrite, although the latter forms over a very narrow temperature range after prolonged heat-treatment. They were also intended to provide further verification of the theory for Widmanstätten ferrite nucleation and growth.

## **10.4 Results**

Fig. 10.4 shows the calculated TTT diagram for both the alloys. The temperature range in which experiments were carried out also marked in the TTT diagrams. The calculated Widmanstätten ferrite, bainite and martensite temperatures are given in Table 10.2.

## 10.4.1 General Microstructure and Morphology

Fig. 10.5 shows that Widmanstätten ferrite plates formed within the prior austenite grains, these are classic lenticular plate shaped with the curved ends because of constraints by the matrix due to the minimisation of the strain energy associated by the formation of these plates. The non parallel formation of these plates suggested that during the initial stage, they nucleate at intragranular nucleation sites such as inclusions and in the latter stage more plates nucleated by the sympathetic nucleation on the existing ferrite plates as shown in Fig. 10.6. It should be noted that these plates are formed in the body of the austenite grains. It is not a section effect produced by primary or secondary Widmanstätten ferrite plates

Identification	Heat-treatment
A1-1	1100 °C @ 15 min $\rightarrow$ 680 °C @ 264 h $\rightarrow$ water quench
A1-2	1100 °C @ 15 min $\rightarrow$ 680 °C @ 600 h $\rightarrow$ water quench
A1-3	1100 °C @ 15 min $\rightarrow$ 700 °C @ 53 h $\rightarrow$ water quench
A1-4	1100 °C @ 15 min $\rightarrow$ 700 °C @ 100 h $\rightarrow$ water quench
A1-5	1100 °C @ 15 min $\rightarrow$ 700 °C @ 144 h $\rightarrow$ water quench
A1-6	1100 °C @ 15 min $\rightarrow$ 700 °C @ 216 h $\rightarrow$ water quench
A1-7	1100 °C @ 15 min $\rightarrow$ 720 °C @ 120 h $\rightarrow$ water quench
A1-8	1100 °C @ 15 min $\rightarrow$ 720 °C @ 346 h $\rightarrow$ water quench
A1-9	1100 °C @ 15 min $\rightarrow$ 740 °C @ 240 h $\rightarrow$ water quench
A1-10	1100 °C @ 30 min $\rightarrow$ 680 °C @ 264 h $\rightarrow$ water quench
A1-11	1100 °C @ 30 min $\rightarrow$ 700 °C @ 264 h $\rightarrow$ water quench
A1-12	1100 °C @ 30 min $\rightarrow$ 720 °C @ 264 h $\rightarrow$ water quench
A1-13	1100 °C @ 30 min $\rightarrow$ 740 °C @ 264 h $\rightarrow$ water quench
A1-14	1300 °C @ 15 min $\rightarrow$ 680 °C @ 264 h $\rightarrow$ water quench
A1-15	1300 °C @ 15 min $\rightarrow$ 740 °C @ 264 h $\rightarrow$ water quench
A2-1	1100 °C @ 15 min $\rightarrow$ 680 °C @ 600 h $\rightarrow$ water quench
A2-2	1100 °C @ 15 min $\rightarrow$ 700 °C @ 600 h $\rightarrow$ water quench
A2-3	1100 °C @ 15 min $\rightarrow$ 720 °C @ 240 h $\rightarrow$ water quench
A2-4	1100 °C @ 15 min $\rightarrow$ 740 °C @ 240 h $\rightarrow$ water quench
A2-5	1100 °C @ 30 min $\rightarrow$ 680 °C @ 264 h $\rightarrow$ water quench
A2-6	1100 °C @ 30 min $\rightarrow$ 700 °C @ 264 h $\rightarrow$ water quench
A2-7	1100 °C @ 30 min $\rightarrow$ 720 °C @ 264 h $\rightarrow$ water quench
A2-8	1100 °C @ 30 min $\rightarrow$ 740 °C @ 264 h $\rightarrow$ water quench
A2-9	1300 °C @ 15 min $\rightarrow$ 680 °C @ 264 h $\rightarrow$ water quench
A2-10	1300 °C @ 15 min $\rightarrow$ 740 °C @ 264 h $\rightarrow$ water quench

Table 10.2: Heat-treatment schedules.

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Table 10.3: Calculated transformation temperatures (°C) /Bhadeshia, 1981a, 1981b, 1981c; Bhadeshia and Edmonds, 1980].

	$Ae_3$	$Ae'_3$	$W_S$	$B_S$	$M_S$
A1	812	773	700	477	338
A2	818	777	700	469	324

originating from austenite grain boundaries or grain boundary allotriomorphic ferrite, above or below the plane of polishing. They were never seen to cross the austenite grain boundaries. These intragranularly nucleated ferrite plates can cross pearlite-austenite boundaries as shown in Fig. 10.7. It can be noted that the plate has sharp boundaries in austenite region while plate boundaries has disappeared in pearlite region, suggesting that pearlite has nucleated from these ferrite plate.

# 10.4.2 Effect of Transformation Temperature

The isothermal transformation temperature play an important role in determining the ambient temperature microstructure. This is clear from the micrographs shown in Fig. 10.8, all specimens were austenitised at 1100 °C for 15 minutes and isothermally transformed at various temperatures. It is depicted from Fig. 10.8, that these plates only form in a particular vicinity of the temperature range but below the  $W_S$  temperature for the alloy concerned, above this temperature grain boundary allotriomorphic ferrite grow and less number of plates were observed. While temperature at below 700  $^{\circ}$ C pearlite was formed in both the alloys as shown in Figure 10.11. Intragranular ferrite plates are often grouped in star-like and more complex configurations at lower reaction temperatures. The transformation temperature also affects the size and number of these plates. At higher transformation temperatures these plates are longer than those observed at the low temperatures as shown in Fig. 10.9a. The thickness of these plates is also very much dependent on the transformation temperature; as the transformation temperature decreases the thickness of these plates also increases Fig. 10.9b.

# 10.4.3 Effect of Transformation Time

In order to examine the effect of transformation time on the progress of transformation and on the morphology of these plates and to ensure that the plates are not a result of the transformation during cooling, specimens were quenched after transforming to various transformation time periods. It is clear that in the early stages of the reaction grain boundary allotriomorphs appeared on the prior austenite grain boundaries, and with the passage of time these allotriomorphs grow along the austenite boundaries and form a continuous layer of ferrite. Further increase in the transformation time does not effect grain boundary allotriomorphs very much but the nucleation of ferrite plates occurs within the body of the austenite grains as shown in the micrographs in Fig. 10.10a.

#### 10.4.4 Effect of Austenitisation Temperature

The effect of austenitisation temperature is to control the austenite grain size, thus providing a large surface to volume ratio (Fig. 9.11). The austenitisation temperature influences both the transformation products and the morphology of these plates. The volume fraction of grain boundary allotriomorphic ferrite clearly decreases with larger austenite grain size. This promotes the subsequent intragranular nucleation of plates of ferrite. Thus, in the specimens austenitised at 900 or 1000 °C, the smaller austenite grain size has suppressed intragranular nucleation and only grain boundary allotriomorphic ferrite grains formed.

#### **10.4.5** Transmission Electron Microscopy (TEM)

Using Transmission electron microscopy it was possible to find inclusions within some of ferrite plates (Fig. 10.12), inclusions which were presumably responsible for the heterogeneous intragranular nucleation of ferrite plates. The probability of observing such nucleation sites is rather small, so that inclusions need not be observed in all the plates even though they may be present. The plates have an apparent length of gently curved boundaries to giving the lenticular outline of the plates (Fig. 10.13). The tips of the plates were also found to be smoothly curved (Fig. 10.14). These morphological observation are consistent with the displacive mechanism in which the lenticular plates shape of ferrite arises through the need to minimise the strain energy associated with the shape deformation. These observations are inconsistent with the growth involving a ledge mechanism since the  $\alpha/\gamma$ interface is certainly not found to be facetted in any way.

## **10.5 Discussion**

A selected set of metallographic results are discussed here, to illustrate the fact that the heat treatment leads first to the growth of polycrystalline layers of allotriomorphic ferrite at the austenite grain surfaces, followed after a time lag, by the intragranular nucleation and growth of Widmanstätten ferrite. More extensive data were collected for alloy A1, which is discussed first. The results are presented in Fig. 10.10c, which shows that the first six days (144 h) of the heat treatment at 700 °C are used up in forming the allotriomorphic layers and that this is followed by the profuse precipitation of intragranularly nucleated Widmanstätten ferrite. With very few exceptions (Fig. 10.10d), the allotriomorphs themselves do no seem to stimulate the growth of secondary Widmanstätten ferrite plates, probably because they are in the wrong crystallographic orientation§ and because of the solute diffusion field associated with their growth (austenite stabilising elements are expected to be displaced into the matrix as the ferrite grows). In fact, there appeared to be a "precipitate-free zone" along the vast majority of the allotriomorphic ferrite/austenite interface (Fig. 10.15).

Theory indicates that in alloy A1, Widmanstätten ferrite should form only over a very narrow temperature range, approximately 690–700 °C, as illustrated in Fig. 10.4. Consistent with this, isothermal transformation at 680 °C produced a microstructure consisting mostly of allotriomorphic ferrite and pearlite, with very few plates of Widmanstätten ferrite (Fig. 10.8a). Plenty of Widmanstätten ferrite plates were however, found after transformation at 720 °C (Fig. 10.8b) and although this is in slight disagreement with the calculated transformation temperature range, examination of the 740 °C sample (Fig. 10.8d) shows clearly that the amount of Widmanstätten ferrite decreases as the temperature increases.

Quantitative metallographic measurements confirm these general trends; to make the measurements easier, the time at the austenitising temperature of 1100 °C was increased from 15 to 30 min (samples A1-10 to A1-13). The abrupt appearance of Widmanstätten ferrite after a long incubation time is also confirmed by the histogram presented in Fig. 10.16a, which represents a quantitative analysis of the number of Widmanstätten ferrite plates counted per unit area of sample,

<sup>§</sup> Widmanstätten ferrite, because of its displacive growth mechanism, always has an orientation relationship with the parent austenite, which is close to the classical Kurdjumov-Sachs or Nishiyama-Wasserman relationships. Consequently, secondary Widmanstätten ferrite plates can only develop if the allotriomorph from which they grow happens to have such an orientation.

using optical microscopy at a magnification of  $\times 100$ . Consistent with the general "C" shape of the Widmanstätten ferrite TTT curve (Fig. 10.4), both the maximum length (Fig. 10.16b) and the number density of Widmanstätten ferrite plates (Fig. 10.16c), show peaks in plots versus the transformation temperature.

Experiments using Alloy A2 revealed the same general trends, with the exception that the rate of reaction decreased in all respects, Fig. 10.16. This is consistent with the known effect of molybdenum in retarding the reaction rate, and it is notable that the retardation is evident in spite of the fact that alloy A2 has a somewhat larger oxygen concentration, corresponding to a larger oxide particle density. It is the oxides which seem to provide sites for the heterogeneous nucleation of Widmanstätten ferrite. This latter point is extremely difficult to prove on a statistical basis because of the very small probability of observing an inclusion in a plate of ferrite [Bhadeshia, 1989], but supporting evidence was nevertheless gathered using carbon extraction replicas for transmission electron microscopy. Fig. 10.17 shows an example where it can be reasonably claimed that clusters of Widmanstätten ferrite plates radiate in many directions from an inclusion. Microanalysis of the inclusions extracted on the replica indicate that they are predominantly aluminium oxides. The mean chemical composition of the inclusions are given in Table 10.4.

Inclusion No.	EDX analysis (wt. %)					
	Fe	Si	Mn	Al		
A1-12	5.6	53.3	—	41.0		
A1-8	35.1	58.1	4.3	2.3		
A1-8	2.2	1.0	_	96.76		

Table 10.4: Average chemical compositions of the three inclusions analysed.

#### **10.6** Conclusions

A method has been developed to refine the microstructure of clean, highstrength martensitic steels by partitioning the austenite grain structure with intragranularly nucleated plates of Widmanstätten ferrite. The plates were induced to nucleate heterogeneously on oxide particles present in the steels, by first forming uniform, thin layers of inactive allotriomorphic ferrite at the austenite grain surfaces. This effectively removed the austenite grain boundaries as potential sites for
the nucleation of Widmanstätten ferrite, which consequently nucleated intragranularly on oxide particles, with ferrite plates radiating in many directions from the oxide particles in such a way as to subdivide the remaining austenite into fine blocks. Quenching after this partial transformation to allotriomorphic and Widmanstätten ferrite resulted in the martensitic decomposition of the blocks of residual austenite, leading to a generally very refined overall microstructure.

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Fig. 10.1: Schematic illustration of the proposed method of refining the martensitic microstructure with intragranularly nucleated plates of Widmanstätten ferrite.



Fig. 10.2: Schematic illustration of the heat treatments used. (a) Variation of isothermal transformation time. (b) Variation of isothermal transformation temperature. (c) Effect of austenitisation temperature.



Fig. 10.3: Schematic illustration of how the double intersection of the  $G_{max}$  curve with the nucleation function  $G_N$  leads to a splitting of the displacive C-curve into two regions, one for Widmanstätten ferrite and the other for bainite. (a) Represent the case where nucleation of Widmanstätten ferrite or bainite is possible over the whole temperature range, hence both Widmanstätten ferrite and bainite exhibit a single TTT curve and (b) is the case where the nucleation of displacive transformation products is not possible between the temperatures A and B, and hence TTT diagram splits into two C-curves, one for Widmanstätten ferrite and the other one for bainite.

x = 5







For alloy A2

Fig. 10.4: Calculated TTT diagrams for the two steels used in the present study.

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Fig. 10.5: Optical micrographs showing the formation of Widmanstätten ferrite plates in alloys (a) A1 and (b) A2. 1100 °C @ 15 min  $\rightarrow$  700 °C @ 9 days.



Fig. 10.6: Optical micrographs showing the sympathetic nucleation of Widmanstätten ferrite plates in alloys A2 (A2-2).



Fig. 10.7: An illustration of a pearlite colony growing around a intragranularly nucleated Widmanstätten ferrite plate (A2-1).



Fig. 10.8: Continued .....



(d)

(c)

Fig. 10.8: Effect of transformation temperature on the formation of intragranular Widmanstätten ferrite plates. All specimens were austenitised at 1100 °C for 15 min and isothermally transformed at (a) 680 °C @ 11 days (b) 700 °C @ 9 days (c) 720 °C 346 @ hr (d) 740 °C @ 10 days.



Fig. 10.9: Effect of transformation temperature on the size, distribution and thickness of intragranular Widmanstätten ferrite plates. All specimens were austenitised at 1100 °C for 15 min and isothermally transformed at (a) 720 °C @ 346 hr (b) 740 °C @ 10 days.



Fig. 10.10: Continued .....



(d)

Fig. 10.10: Effect of transformation time on the formation of intragranular Widmanstätten ferrite plates. All specimens were austenitised at 1100 °C for 15 min and isothermally transformed at 700 °C for (a) 53 hr (b) 100 hr (c) 6 days (d) 9 days.



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(a)



(b)

Fig. 10.11: Continued .....



(d)

Fig. 10.11: Effect of austenitisation temperature on the formation of intragranular Widmanstätten ferrite plates. Specimens were isothermally transformed at 740 °C for 10 days after austenitisation for 15 min at (a) 1100 °C (b) 1300 °C and 680 °C for 11 days after 15 min of austenitisation at (c) 1100 °C (d) 1300 °C.



Fig. 10.12: Replica electron micrograph of an inclusion of the type which were presumably responsible for the intragranular nucleation of Widmanstätten ferrite plates.



(a)

Fig. 10.13: TEM micrograph showing the autocatalytic nucleation of intragranularly nucleated Widmanstätten ferrite plates.



Fig. 10.14: TEM micrographs showing that intragranularly nucleated plates have smoothly curved lenticular plate morphology.



Fig. 10.15: Optical micrograph showing a precipitate free zone between the grain boundary allotriomorphic ferrite layers and intragranularly nucleated Widmanstätten ferrite plates.



Fig. 10.16: Continued .....



# (c)

Fig. 10.16: (a) Histogram showing the number of Widmanstätten ferrite plates per unit area, counted on metallographic samples observed using optical microscopy at a magnification of  $\times 100$ , as a function of the time at an isothermal transformation temperature of 720 °C. (b) Length of the longest plate observed on a random section, as a function of the isothermal transformation temperature after holding at temperature for 264 hr. (c) Number of plates per unit area, as a function of the transformation temperature after holding at temperature for 264 hr.



Fig. 10.17: Carbon extraction replica micrograph showing plates of Widmanstätten ferrite apparently emanating from an inclusion nucleation site.

# Chapter 11 REAUSTENITISATION IN HIGH STRENGTH HARDENABILITY STEEL

There is now a need to conduct urgent experiments on the reaustenitisation behaviour of steels as an aid to the modelling of microstructure in welds. In multilayer weld deposits, the heat input associated with the deposition of new layers, reheats the underlying microstructure to temperatures where austenite formation can occur. The new austenite then cools and transforms back to a microstructure which can be rather different from that obtained immediately after weld deposition. Because many of the alloys used in the deposition of high-strength welds are designed to transform ultimately into bainitic microstructures, it is useful to study the reaustenitisation process by heating such microstructures. This chapter deals with the reaustenitisation process from a starting microstructure which is a mixture of bainite and residual austenite. The term residual austenite is used to represent the austenite which is left untransformed at the temperature where bainite is allowed to grow. Particular emphasis is placed on the mechanism and the kinetics of reaustenitisation process.

# **11.1 Material Selection**

The steel selected for the present study is one which contains high silicon and manganese concentrations as the major alloying elements. The silicon retards the growth of cementite, so that a microstructure of just bainitic ferrite and residual austenite can be obtained by the transformation of austenite below the bainite-start  $(B_S)$  temperature [Hehemann, 1970]. Such alloys are becoming more prominent in industry, both as wrought materials [Bhadeshia and Edmonds, 1979] and in the form of high silicon cast irons [Rundman *et al.* 1988]. Manganese and molybdenum increase the incubation time for the formation of diffusional transformation products such as allotriomorphic ferrite, and generally raise the hardenability of the steel. The detailed chemical composition of the steel used in the present study is given in Table 11.1.

Table 11.1: Chemical composition of the steel used in the present study.

Steel	Chemical Composition (wt. %)						
	C	Si	Mn	Mo	Ti	Al	O (ppm)
A2	0.22	2.05	3.07	0.7	0.004	0.005	94

# **11.2 Experimental Procedures**

## 11.2.1 Heat Treatments

High speed dilatometry was utilised to study the kinetics of reaustenitisation. All the samples were homogenised at 1250 °C for 3 days prior to dilatometric experiments, as discussed in Chapter 3 along with the other details of the heat treatment techniques. All heat treatments were performed in a Theta Industries high-speed dilatometer using homogenised, high purity, high hardenability steel, austenitised at 900 °C for 5 minutes, isothermally transformed at a temperature  $T_i = 400$  °C for 2000 s to get a mixture of bainitic ferrite plus residual austenite and then, instead of cooling the specimens to ambient temperature, they were heated rapidly to an elevated temperature  $T_{\gamma}$  for isothermal reaustenitisation. The specimens were not cooled below 400 °C, in order to avoid the martensitic decomposition of the austenite. Schematic diagrams of the heat treatment cycles have already been shown in Fig. 3.1.

#### 11.2.2 Microscopy

Specimens for optical and transmission electron microscopy were obtained from heat treated samples and prepared as discussed in Chapter 3. Thin foil samples were examined using a PHILIPS EM400T transmission electron microscope, equipped with a LINK EDX system to facilitate energy

#### 11.3 Results

The general microstructure is illustrated in Fig. 11.1, and as expected, consisted of a mixture of bainitic ferrite, retained austenite and some martensite resulting from the decomposition of the residual austenite after cooling from the bainite formation temperature.

#### 11.3.1 Dilatometry

The first detectable growth of austenite was found to occur at 660 °C as illustrated in Fig. 11.2, note that a length contraction is expected as ferrite transform to austenite. In all cases the transformation rate was initially rapid, but decreased with time at the isothermal reaustenitisation temperature  $T_{\gamma}$  so that the specimen length eventually stopped changing. The maximum relative length change as a function of  $T_{\gamma}$  is plotted in Fig. 11.3. The results showed that  $\frac{\Delta L}{L}$  increases as  $T_{\gamma}$ increases from 660 °C to 740 °C and then remains essentially constant with the further increase in  $T_{\gamma}$  to 860 °C. The maximum degree of transformation to austenite thus increases from nearly zero at 620 °C to complete reverse transformation at

above 740 °C. It is also seen from the Fig. 11.3, that the rate of ferrite to austenite transformation increases with  $T_{\gamma}$ .

#### 11.3.2 Transmission Electron Microscopy

The phenomenon of reaustenitisation can be monitored by observing the thickening of austenite layers using transmission electron microscopy (Figs. 11.4-11.11). Fig. 11.5 shows micrograph for reaustenitisation at 660 °C in which the ferrite subunits are parallel to each other and are separated by the austenite layers (now become martensite after cooling to ambient temperature). The thickness of the austenite films does not seem to increase significantly at 660 °C as expected from the dilatometric results (Fig. 11.3). As the isothermal reaustenitisation temperature increases, the austenite films become detectably thicker (Figs. 11.6-11.8). However the austenite layers still retain their general form as shown in Fig. 11.8 for reaustenitisation at 740 °C. Fig. 11.9 shows that there is some ferrite retained even after reaustenitisation at 780 °C. The electron micrographs in Figs. 11.10 and 11.11 demonstrate completely martensitic structures, indicating the completion of austenitisation following the 820 and 860 °C heat treatments This also confirms the dilatometric data (Fig. 11.3), that the maximum length change achieved beyond about 780 °C does not vary much with  $T_{\gamma}$ . A slight decrease is in fact expected as  $T_{\gamma}$  rises, even though the samples fully reaustenitise, because the difference in austenite and ferrite densities decreases with rising temperature.

#### 11.3.3 Microanalysis

The microanalysis results are given in Table 11.2 and Figs. 11.12-11.16 illustrate the results from a range of isothermal reaustenitisation temperatures. They show that the degree of partitioning substitutional of alloying elements decreases with increasing austenitisation temperature.

#### 11.3.4 Hardness

The hardness of each specimen was measured after the isothermal reaustenitisation and the results are plotted in Fig. 11.17. The results show that the hardness achieves a maximum value after austenitisation at about 780  $^{o}$ C.

Table 11.2: EDX analysis of the (a) matrix and (b) ferrite. (All the specimens were austenitised at 900 °C for 5 min and then transformed to bainite at 400 °C for 2000 s prior to reaustenitisation).

Temperature	EDX analysis (wt. $\%$ )					
°C	Fe	Mn	Si	Mo		
620	$93.7 \pm 1.2$	$3.4\pm0.7$	$2.1\pm0.2$	$0.6\pm0.3$		
660	$93.6\pm0.7$	$3.3\pm0.5$	$2.1\pm0.4$	$0.9\pm0.5$		
680	$94.2\pm0.7$	$3.3\pm0.4$	$1.9\pm0.4$	$0.6\pm0.3$		
700	$94.1\pm0.7$	$3.4\pm0.6$	$1.9\pm0.4$	$0.6\pm0.5$		
860	$94.1\pm0.6$	$3.2\pm0.3$	$1.9\pm0.1$	$0.7\pm0.4$		

(a)

(b)

Temperature	EI			
°C	Fe	Mn	Si	Mo
620	$94.1\pm0.7$	$2.7\pm0.5$	$2.3\pm0.3$	$0.9\pm0.7$
660	$95.0\pm0.9$	$2.4 \pm 0.4$	$2.0 \pm 0.4$	$0.5\pm0.6$
680	$95.1\pm0.9$	$2.3\pm0.4$	$1.9\pm0.4$	$0.6\pm0.3$
700	$94.6\pm0.7$	$2.5\pm0.8$	$2.1\pm0.5$	$0.7\pm0.5$
860	$94.5\pm0.7$	$2.4 \pm 0.3$	$2.1\pm0.2$	$0.9\pm0.7$

Table 11.3: Effect of reaustenitisation temperature on partition coefficient.

Temperature	Partition Coefficient $[K_i = \frac{K_i(\gamma)}{K_i(\alpha)}]$ (wt. %)				
°C	Mn	Si	Mo		
620	1.2	0.9	0.7		
660	1.3	1.0	1.7		
680	1.4	0.9	0.9		
700	1.3	0.9	0.9		
860	1.3	0.9	0.7		

# **11.4 Discussion**

The results obtained in this study generally confirm the earlier published [Yang, 1987; Yang and Bhadeshia, 1987, 1990] on] experiments but provide additional microstructural detail. The Yang and Bhadeshia model shows that because isothermal transformation of austenite to bainite ceases prematurely before the austenite

achieves its equilibrium carbon concentration, there is a large temperature hysteresis before the reverse transformation to austenite become possible during heating from the bainite transformation temperatures. Any reverse transformation to austenite cannot occur until the sample is heated to an elevated temperature where the residual austenite composition becomes identical to the composition given by the  $Ae'_3$  phase boundary. This leads to a large hysteresis in the forward and reverse transformation temperatures for austenite, a hysteresis which is not found when the starting microstructure is instead a mixture of allotriomorphic ferrite and austenite [Tsuzaki *et al.* 1980]. This is evident from TEM micrographs with increasing thickness of austenite layers as shown in Fig. 11.18. A close examination of Fig. 11.19 shows that austenite layers become thicker they retain their layer like morphology between the ferrite sub units. This provides strong evidence that austenite grows by the normal movement of the approximately planar  $\alpha/\gamma$  interface as assumed by Yang [1987].

## 11.4.1 EDX Analysis

The results of energy dispersive X-ray analysis of isothermally reaustenitised specimens show that the degree of partitioning of substitutional alloying elements, as indicated by the deviation of the partition coefficient  $K_i$  from unity, where

$$K_i = \frac{x_i^{\gamma}}{x_i^{\alpha}} \tag{11.1}$$

decreases with increasing reaustenitisation temperature (Fig. 11.16). As the driving force for reaustentisation increases, the transformation tends towards paraequilibrium or negligible partition-local equilibrium; this is illustrated clearly by the data for 700 °C. The concepts of paraequilibrium and local equilibrium have been discussed in Chapter 1. Paraequilibrium is state of constrained equilibrium in which the substitutional lattice is configurationally frozen with respect to the transformation interface. Hence, even though the transformation is diffusional in nature, the ratio (atom fraction of substitutional element (i)/atom fraction of iron) is the same in  $\alpha$  and  $\gamma$ . Thus, the chemical potentials of the substitutional elements are not equal in the two phases. Carbon, which can diffuse faster, reaches equilibrium subject to this constraint. In negligible-partioning-local equilibrium (NPLE), equilibrium is maintained for all the transformation interface, but the concentration of substitutional element is essentially the same in all phases. The results also show that as thickness of the austenite layers increases with time at for a given  $T_{\gamma}$ , the partition coefficient  $K_i$  changes indicating that the concentrations of alloying

elements at the interface during the growth of austenite are not equilibrium concentrations. These results are qualitatively consistent with the dilatometric data. One of the factors for the increased rate of transformation at high  $T_{\gamma}$  is the fact that the degree of redistribution of alloying elements during transformation decreases with increasing  $T_{\gamma}$ .

## 11.4.2 Carbon Concentration of the Residual Austenite

The carbon content of the residual austenite when isothermal transformation ceases is very useful in understanding the transformation mechanism. Because of the relatively high silicon concentration in the steel used, the precipitation of cementite tends to be rather sluggish. Consequently, isothermal transformation to upper bainite generates a microstructure consisting of carbide-free bainitic ferrite and carbon-enriched residual austenite. It is then possible to estimate the carbon concentration  $x_{\gamma}$  of the residual austenite using a simple mass balance procedure, if the volume fraction of bainitic ferrite  $V_b$  is known

$$x_{\gamma} = \frac{\overline{x} - V_b \times x_{\alpha}}{1 - V_b} \tag{11.2}$$

where  $\overline{x}$  is the average carbon concentration of the alloy and  $x_{\alpha}$  is the carbon concentration of the bainitic ferrite. The volume fraction  $V_b$  can be calculated from the dilatometric data as discussed by Bhadeshia [1982]. The values of  $x_{\gamma}$  estimated by using the procedures just described here, for the point where isothermal transformation ceases at any given temperature, are plotted on the phase diagram presented in Fig. 11.20. The phase boundaries were calculated using the method given by Bhadeshia and Edmonds [1980]. The data presented in Fig. 11.20 confirm that the formation of upper bainite stops prematurely, well before the carbon concentration of the residual austenite reaches the paraequilibrium  $Ae'_3$  phase boundary. This effect is known as the "incomplete reaction phenomenon" [Bhadeshia, 1985, Christian, et al. 1984]. After isothermal transformation to bainite at the temperature  $T_b$  has ceased, if the sample is rapidly heated to an isothermal temperature  $T_\gamma$ for reaustenitisation, the reverse transformation to austenite does not require any nucleation, simply the movements of already existing ferrite-austenite interfaces. Because the bainitic ferrite consist of ferrite sub units which are approximately parallel to each other. The thickness of austenite films measured by stereology is given in Fig. 11.18, which shows that as the reaustenitisation temperature increases the austenite films between bainitic ferrite become thicker and eventually consume

 $<sup>\</sup>S$  The incomplete reaction phenomenon has been discussed in detail in chapter 4.

all the bainitic ferrite transformed to austenite i. e., above 780 °C. This is also confirmed by the transmission electron microscopy.

## 11.4.3 Macrohardness

The hardness of the reaustenitised samples after quenching to ambient temperature has been found to initially increase as with the isothermal reaustenitisation temperature. This increase is expected since the amount of austenite (and hence martensite at austenitisation temperature) increases with  $T_{\gamma}$ . The maximum value of about 600 HV observed at around 780 °C beyond which sample becomes fully austenitic is more difficult to understand, but could arise because samples quenched from higher temperature undergo a greater degree of auto tempering of the martensite.

#### 11.5 Theory for Reaustenitisation

In this section the thermodynamic model presented by Yang and Bhadeshia [1987] for the interpretation of the observations on reaustenitisation from a starting microstructure of bainite and retained austenite are analysed in the light of the results obtained in the present study. Since after the diffusionless growth of bainite, carbon is rapidly and spontaneously redistributed into the residual austenite with an accompanying reduction in free energy, the  $\alpha_b/\gamma$  transformation in its original form is irreversible. The problem of reaustenitisation is therefore considerably different from the case of martensite to austenite in for example, shape memory alloys. It is noted that the formation of bainite ceases prematurely during isothermal transformation when the carbon content of the residual austenite reaches the  $T'_o$  curve (the phase diagram for the alloy is presented in Fig. 11.20). It follows that the carbon concentration  $x_{\gamma}$  of the residual austenite when the formation of bainite cease at  $T_b$ , is given by (point marked 'a' in Fig. 11.20)

$$x_{\gamma} = x_{T_a}'[T_b] \tag{11.3}$$

furthermore, it is noted that:

$$x_{\gamma} \ll x_{Ae_{a}'}[T_{b}] \tag{11.4}$$

where  $x_{Ae'_3}[T_b]$  is marked "b" in Fig. 11.20. Thus, although the formation of bainite ceases at, because  $x_{\gamma} \ll x_{Ae'_3}[T_b]$ , the driving force for austenite to transform diffusionally to ferrite is still negative. Another way of expressing this is to say that the volume fraction of bainite present when its formation ceases at  $T_b$  is much

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less than is required by the Lever rule. In fact, this remains the case until the temperature T is high enough *i.e.*,  $T = T_{\gamma}$  to satisfy the equation:

$$x_{\gamma} = x_{Ae_a'}[T_b] \tag{11.5}$$

Hence, reaustenitisation will first occur at a temperature  $T_{\gamma}$ , as indicated in Fig. 11.20 (marked c), and as observed experimentally. Note that this is a direct consequence of the mechanism of the bainite transformation, which does not allow the transformation to reach completion. The theory goes further than explaining just the temperature at which the reverse transformation should begin. It also predicts that any temperature T greater than  $T_{\gamma}$ , the reverse  $\alpha \to \gamma$  transformation should ceases as soon as the residual austenite carbon concentration  $x'_{\gamma}$  (initially  $x_{\gamma}$  reaches the  $Ae'_{3}$  curve, i.e., when

$$x'_{\gamma} = x_{Ae'_{3}}[T_{\gamma}] \tag{11.6}$$

with the equilibrium volume fraction of austenite (at the temperature  $T_{\gamma}$ ),  $V_{\gamma}$ , being given by:

$$V_{\gamma}[T_{\gamma}] = \frac{\overline{x}}{x_{Ae'_3}}[T_{\gamma}] \tag{11.7}$$

assuming that the carbon concentration of ferrite is negligible and  $x_{Ae'_3}[T_{\gamma}] > \overline{x}$ when  $x_{Ae'_3}[T_{\gamma}] = \overline{x}$ , the alloy eventually becomes fully austenitic (point 'd' in Fig. 11.20) and If this condition is satisfied at  $T = T_{\gamma}$  then all  $T > T_{\gamma}$ , the alloy transform completely to austenite. These concepts immediately explain the dilatometric data in which the degree of  $\alpha \to \gamma$  transformation increase (from zero at 660 °C with the temperature of isothermal reaustenitisation, until the temperature 780 °C where the alloy transforms completely to austenite. The results obtained in present study thus generally confirm the Yang and Bhadeshia model for reaustenitisation of mixtures of bainitic ferrite plus residual austenite.

#### **11.6** Conclusions

The kinetics of reaustenitisation in relatively high silicon concentrations has been studied by a combination of techniques such as high speed dilatometry, transmission electron microscopy, EDX analysis, stereology and macro hardness. It is found that the formation of austenite increases with increasing reaustenitisation temperatures and at 780 °C all the bainitic ferrite transformed to austenite. The transformation is initially rapid but slow at the end of reaction. The formation

of austenite was found to take place by the movements of planar ferrite/austenite interfaces. It is confirmed by measuring the thickness of the austenite films which increase during the reaustenitistion process. The results are generally consistent with the theory of reaustenitisation as proposed be Yang and Bhadeshia.

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Fig. 11.1: Typical mixed microstructure of bainitic ferrite, retained austenite and martensite after isothermal transformed at  $400 \, ^{\circ}C$  for  $2000 \, \text{s}$  followed by water quenching. a) Optical micrograph. b) TEM micrograph.



Fig. 11.2: Continued .....



Fig. 11.2: Isothermal reaustenitisation studied using dilatometry. The specimens were initially isothermally transformed to bainite at 400 °C for 2000 s and then rapidly heated to the isothermal reaustenitisation temperature indicated on each figure.



Fig. 11.3: The maximum magnitude of the relative length change  $\left(\frac{\Delta L}{L}\right)$  increases with the reaustenitisation temperature  $(T_{\gamma})$  and then attains an approximately constant value after the sample can achieved a fully austenitic state. Note that all the length changes are in fact negative.



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Fig. 11.4: Microstructure of the specimen isothermally reaustenitised at  $620 \, ^{\circ}C$  for 2000 s. Note that there is some rounding of the bainite sub-units at their tips.



Fig. 11.5: Microstructure observed at  $T_{\gamma} =$  660 °C for 3000 s.




Fig. 11.6: Microstructure observed after isothermal reaustenitisation at 680 °C for 2000 s.



Fig. 11.7: Thickening of the austenite films after reaustenitisation at 700 °C for 3000 s.





Fig. 11.8 : The residual austenite films between bainitic ferrite subunits become thicker after isothermal reaustenitisation at 740 °C for 3000 s.



Fig. 11.9: Showing that although most of the microstructure reaustenitised but still some of the ferrite subunits are present after isothermal reaustenitistion at 780  $^{\circ}C$  for 3000 s.



Fig. 11.10: Microstructure observed after reaustenitistion at 820  $^{o}C$  for 3000 s.



Fig. 11.11: Showing that specimen completely reaustenitised after isothermal transformation at 860 °C for 3000 s.



Fig. 11.12: Microanalytical data obtained using energy dispersive X-ray analysis on PHILIPS 400T ( $T_{\gamma} = 620$  °C).



Fig. 11.13: Microanalytical data obtained using energy dispersive X-ray analysis on PHILIPS 400T ( $T_{\gamma} = 660 \ ^{\circ}C$ ).



Fig. 11.14: Microanalytical data obtained using energy dispersive X-ray analysis on PHILIPS 400T ( $T_{\gamma} = 700 \ ^{\circ}C$ ).

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Fig. 11.15: Microanalytical data obtained using energy dispersive X-ray analysis on PHILIPS 400T ( $T_{\gamma} = 860 \ ^{o}C$ ).



Fig. 11.16: The effect of reaustenitisation temperature on the partition coefficient of manganese, showing that the degree of partitioning of manganese increases as the reaustenitisation temperature increases.

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Fig. 11.17: The effect of isothermal reaustenitisation temperature on the bulk hardness of the specimens.



Fig. 11.18: Measurement of the thickness of the residual austenite films. The thickness of austenite films increases with the increasing reaustenitisation temperature.



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 $[T=400 \ ^o\mathrm{C}]$ 



 $[T_{\gamma}=660~^o\mathrm{C}]$ 

Fig. 11.19: Continued .....



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 $[T_{\gamma}=700~^o{\rm C}]$ 

Fig. 11.19: Continued .....



 $[T_{\gamma}=740~^o{\rm C}]$ 

Fig. 11.19: TEM micrographs showing the thickening of austenite films after isothermal reaustenitisation for 3000 s at temperatures indicated on each figure, note that the films remain parallel to the ferrite sub-units.



Fig. 11.20: Calculated phase diagram with experimental data of carbon concentration of residual austenite at the termination of isothermal transformation. The para-equilibrium phase boundaries  $Ae'_3$  and  $T_0$  calculated as in [Bhadeshia and Edmonds, 1980].

## Chapter 12 SUGGESTIONS FOR FURTHER WORK

Nucleation Rate for Widmanstätten Ferrite: Some progress has been made in understanding the mechanism of Widmanstätten ferrite and bainite nucleation. Nevertheless, there is no experimental verification of the nucleation *rate*, and quantitative studies need to be pursued with vigour.

Although the linear relationship between the activation energy for nucleation and the chemical free energy change accompanying nucleation has been more or less verified, the slope and intercept of the experimental relation needs to be rigorously compared with theory. This cannot be done without extensive data on for example, dislocation (or interface) mobilities as a function of temperature.

Given the analogy between bainite and acicular ferrite, it should be possible to formulate the kinetic theory for acicular ferrite after accounting for its intragranular nucleation. Experiments are needed to verify the dependence of the activation energy for the nucleation of acicular ferrite on inclusions, on the chemical driving force. In particular, it is necessary to design and study samples in which the ratio of grain surface to intragranular nucleation densities varies. Monitoring the onset of a detectable degree of acicular ferrite formation then enables the free energy dependence to be deduced. It will be necessary to cover a range of alloys to give sufficient variation in the driving force at constant temperature. The theory will then be tested against experimental kinetic data on acicular ferrite in low-alloy steels.

Chaotic Microstructure in Ultrahigh–Strength Steel: One of the most exciting results to emerge from the work was the ability to induce the intragranular nucleation of ferrite plates in wrought steels containing extremely small quantities of nonmetallic particles. The dismantling of packets of parallel ferrite plates in bainitic or martensitic microstructures, into differently orientated chaotic acicular ferrite plates, improves toughness. The increased chaos can only be achieved by introducing inclusions as intragranular nucleation sites. The gain in toughness achieved in this manner overcomes any loss due to the presence of inclusions, in welds and low–strength steels. The same level of inclusions cannot however, be tolerated in ultrahigh–strength (UHS) steels ( $\sigma_Y \geq 1300$  MPa) which typically contain oxygen at < 10 ppm. The research has shown that by eliminating the austenite grain surfaces as potential nucleation sites (by decorating them with a very thin layer of allotriomorphic ferrite), the very small oxygen concentration is sufficient to nucleate acicular ferrite in UHS steel.

However, much further work is needed to make this idea into a viable proposition, since the heat treatments used were not realistic from a commercial point of view. Alloys need to be designed which are able to produce the required microstructure during continuous cooling transformations under near natural cooling conditions.

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