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FEATURES OF BAINITE TRANSFORMATION IN STEELS

ABSTRACT

Some features of bainite transformation in steels are reviewed with the objective of summarising the progress of current schools. A great deal of research has revealed substantial information concerning the mechanism of the bainite transformation in steels. Two competing models regarding the formation of bainite from austenite in steels are reviewed. Four basic controversies concerning the formation of bainite are discussed. They concern the diffusive or displacive mechanism of bainite transformation, the role of carbon diffusion, the surface relief effects and thickening process of bainitic ferrite laths. The review also includes an assessment of modelling of novel ultrahigh bainitic steels.

Key words: bainite transformation, displacive mechanism, diffusive mechanism

INTRODUCTION

Bainite transformation in steels takes place in a broad temperature region, in which thermodynamic and kinetic behaviours vary greatly so that bainite is characterised by miscellaneous morphologies and complicated formation mechanisms. Up to now many topics on bainite transformation, such as the formation mechanism of ferritic component and some details of carbide precipitation process, remain controversial [1, 2].

Bainite seems to be the most complicated microstructure of steel. Therefore it is not wonder that its formation mechanism has been subjected to constant discussion ever since Davenport and Bain studied it in 1930 [3].

In recent years, the argument on the mechanism of the bainite reaction is still continuing based on the thermodynamics and transformation kinetics in steels [4-6].

This paper summarises recent works on the some specific features of the bainitic transformation in steels.

Bainite reaction in the light of the overall classification of phase transformation

All the $\gamma \rightarrow \alpha$ transformations (including bainite reaction) are a first order transformations which occur by the motion of well-defined interfaces*. The structure of the interface influences

*The Ehrenfest classification [7] of phase transformation is based on the successive differentiation of a thermodynamic potential (e.g. Gibbs free energy) with respect to an external variable such as temperature or pressure. The order of the transformation is given by the lowest derivative to exhibit a discontinuity. In first order transformation the partial derivative of the Gibbs free energy with respect to temperature is discontinuous at the transition temperature. In a first order transformation the phase change occurs at a well-defined interface, the interface separating two forms of the parent and product phases. In these circumstances interface structure must dominate the mechanism of transformation and the formation of a new phase involves a nucleation and growth process.

the way in which the atoms of the parent phase (austenite) move in order to generate the ferrite lattice (product phase).

There could be distinguished two main groups of phase transformations in alloys with essential differences between them: *diffusional* and *martensitic transformations* [8-11]. *Diffusional transformations* (also called *reconstructive transformations*) involve the diffusion of all elements, including iron [8].

Many materials other than steel are now known to exhibit the same type of solid-state phase transformation, known as a *martensitic transformation*, frequently also called a *shear transformation* [2, 5, 11]. All *martensitic transformations* involve co-ordinated movements of atoms and are *diffusionless* [2]. *Martensitic transformations* are always interface controlled where both nucleation and growth become diffusionless. There is no mixing up of atoms during transformation, a particular atom of the martensite originated from a corresponding particular atom in the parent crystal [10]. There exists an atomic correspondence between the parent and product lattices.

Solid-state phase transformations in steels can involve both substitutional and interstitial atoms. It is conceivable that the substitutional atoms do not diffuse during transformation whereas the much more mobile interstitial atoms are able to partition between austenite and ferrite. Thus the lattice change could be accomplished by *displacive transformation* as far as the substitutional solute and iron atoms are concerned. When in interstitially alloyed steels the substitutional lattice transforms without diffusion while the interstitials diffuse, this is *displacive transformation* [11].

The extent to which the carbon atoms partition during the growth of ferrite plates by this mechanism can in principle be between equilibrium and full supersaturation (i.e. zero partitioning). The diffusion of interstitials has no influence on the shape change accompanying transformation so that the macroscopic characteristics of martensite are retained.

Martensitic transformations can be regarded as a *diffusionless subset of displacive transformations* [10, 11].

With *displacive* and *martensitic transformations* the product phase always has thin plate morphology since this minimises the strain energy associated with the shape deformation [11].

Incoherent, coherent and semi-coherent boundaries can co-exist around a particle that has grown diffusively. Only semi-coherent and coherent boundaries can exist around a particle that has grown displacively [7].

Bainitic ferrite

The shape of bainitic ferrite on a macroscopic scale can be classified as lath-like, plate-like, granular, or even with nodular external morphology [12-21].

Bainite is a non-lamellar mixture of ferrite, retained austenite and/or carbides that can be obtained in steels by the transformation of austenite in a temperature range delimited approximately by the martensite start temperature M_s^* , and the temperature at which fine pearlite can grow at a reasonable rate. As we will see later, the carbide part of the microstructure is not essential, the carbides form as a secondary reaction, rather as in the tempering of martensite [22-25].

Nucleation of bainite is different from that of allotriomorphic ferrite and it comes from the observation that bainite transformation start temperature B_S decreases at a faster rate with an increase in alloy concentration than is the case for Ae_3 temperature. It was found that

* The definition of the martensite-start temperature is that it corresponds to the temperature where both nucleation and growth become diffusionless.

the activation energy for bainite nucleation is proportional to the driving force available for transformation [26-29], in a manner typical for martensitic transformations [30-34]. The nucleation of bainite occurs with the paraequilibrium* partitioning of carbon, i.e. there is a redistribution of carbon during the formation of the nucleus [26, 27, 35].

Ferrite growth without a change in composition can only occur below the T_0 temperature at which ferrite (α) and austenite (γ) of identical composition have equal free energy [36-38]**. The T_0 temperature lies between the Ae_3 and Ae_1 temperatures that in turn define the upper and lower limits respectively of the two-phase $\alpha + \gamma$ field. For the range $Ae_3 \rightarrow T_0$ growth is only possible if the α has a different composition from the γ , whereas between T_0 and Ae_1 growth of ferrite of equilibrium or unchanged composition is in principle possible. Below the Ae_1 temperature only massive growth is possible if the transformation mechanism is diffusional [5, 6, 8, 11, 39-40].

The ferrite always has a Kurdjumov-Sachs type orientation relationship with the austenite in which it grows [41-45].

The clusters of ferrite plates are known as “sheaves” (Fig. 1); each sheaf is itself in the form of a wedge-shaped plate on a macroscopic scale. The sheaves inevitably nucleate heterogeneously at austenite grain boundaries.

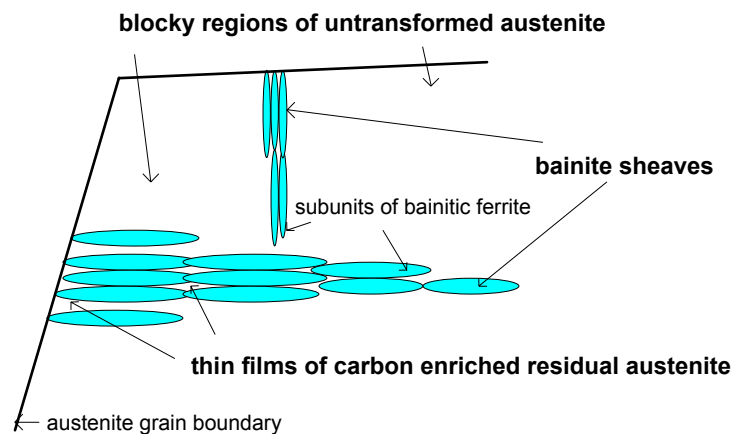


Fig. 1. Evolution of a bainite microstructure

The classification of bainite involves rather complicated problems relating to the constituents of the structures. Due to the variety of nomenclature used for various forms of bainite a confused state of this subject also exists in the literature. Many investigators used a wide variety of terminology to describe observed morphologies, as “granular bainite”, “nodular bainite”, “columnar bainite”, “upper and lower bainite”, “carbide free bainite”, etc. [41-43, 45-51].

* Hultgren [23], introduced the term “paraequilibrium” to describe the constrained equilibrium between two phases which are forced to have the same substitutional to iron atom ratio, but which achieve equilibrium with respect to carbon. Ferrite formation under conditions of paraequilibrium essentially implies that the substitutional lattice is configurationally frozen and transformation occurs at the rate controlled by the diffusion of carbon in the austenite, the driving force for paraequilibrium transformation is dissipated in this process alone.

** The T_0 temperature can be defined [36-38] such that stress free austenite and ferrite of the same composition (with respect to both the interstitial and the substitutional alloying elements) are in metastable equilibrium. Thus any displacive transformation involving a full supersaturation of carbon (i.e. bainitic ferrite would then inherit the carbon content of the parent austenite) can occur only below the appropriate T_0 temperature.

The classifications are based primary on the morphology of ferrite and the morphology and places of cementite particle precipitation during transformation. *Upper bainite* in this case consists of parallel ferrite laths with cementite/and austenite layers between them. The cementite precipitates from the carbon-enriched austenite films between the ferrite plates; the ferrite itself is free from carbides. *Lower bainite* is of the plate-like morphology and involves fine cementite platelets within bainitic ferrite oriented in a specific direction [24].

OVERVIEW OF TRANSFORMATION MECHANISMS

The mechanism of bainite transformation in steels remains still controversial and involves two general hypotheses that bainitic reaction occurs via a diffusional mechanism [1], and that bainitic reaction occurs in a displacive mechanism as far as the substitutional elements are concerned [22].

Diffusive mechanism

During diffusional transformation an interface can move in two ways: atoms may cross all parts of the interface causing it to move as a whole, or they may attach themselves to the product phase only at favourable sites such as steps in which case only the steps move [27, 54-56]. The normal displacement of the stationary part of the boundary then occurs by the passage of such steps across the boundary, the amount of displacement depending on the step height.

Aaronson and Kinsman [57, 58] presented a general condition for predicting whether growth will be continuous or stepped. The occurrence of stepped growth depends on the existence of periodic equilibrium interface configurations whose spacing determines the height of the steps. Kinsman [58] showed that the existence of equilibrium interface configurations also depends on the driving force for transformation, so that stepped growth becomes less likely at the high undercoolings. The exact mechanism is determined by the orientation dependence of interface energy (and hence mobility) and by the driving force for interface motion.

Because atoms are only attached to the product phase at a fraction of the boundary the displacement of the boundary by step motion must be slower than continuous growth in which every element of the interface is displaced simultaneously [6, 40].

Aaronson [57] observed growth ledges on the broad faces of proeutectoid ferrite precipitated from austenite in Fe-C alloys by replica electron microscopy, and suggested that the diffusional growth of these ledges along the broad faces of a new phase resulted in thickening in the direction perpendicular to the broad faces. On the basis of a quantitative discussion on the ledge mechanism [58], Aaronson et al. predicted [58-62] that Widmanstätten and bainitic ferrite would grow by the ledge mechanism. Honeycombe [43], Batte and Honeycombe [63], Mishima [64], and Barbacki [65] also provided some evidence for the ledge mechanism of ferrite formation during eutectoidal decomposition of alloyed austenite.

According to the diffusive mechanism a short-range diffusion of the substitutional atoms is expected to occur at well-developed ledges in the austenite/ferrite interface. It is also proposed that bainitic ferrite grows under full local equilibrium between ferrite and austenite what means that carbon content in ferrite would be prescribed by the $\alpha/(\alpha^{\square} + \gamma)$ boundary in phase diagram.

Displacive mechanism

According to the displacive mechanism, bainite is an aggregate of discrete sub-units of bainitic ferrite produced directly by shear and retained austenite or carbides (cementite) which rather form as a secondary reaction [11, 22, 26, 36, 52, 53].

In any case, the mixture of ferrite plates with retained austenite without carbides is regarded as a special kind of bainite [52, 53].

On the assumption that there is no fundamental difference in the mechanism of bainite reaction between upper and lower bainite if bainitic ferrite when it forms is supersaturated with carbon, there could be constructed a useful model for the transition from upper to lower bainite [49, 52]. The model constructed by Matas and Hehemann [52] and by Bhadeshia [49] involves a comparison between the times needed to precipitate cementite within the bainitic ferrite plates with the time required to decarburise supersaturated ferrite plates. When decarburisation dominates upper bainite is obtained. Alternatively, whereas carbides are precipitated within ferrite plates it leads to the formation of lower bainite. The model is illustrated schematically in Figure 2 [49].

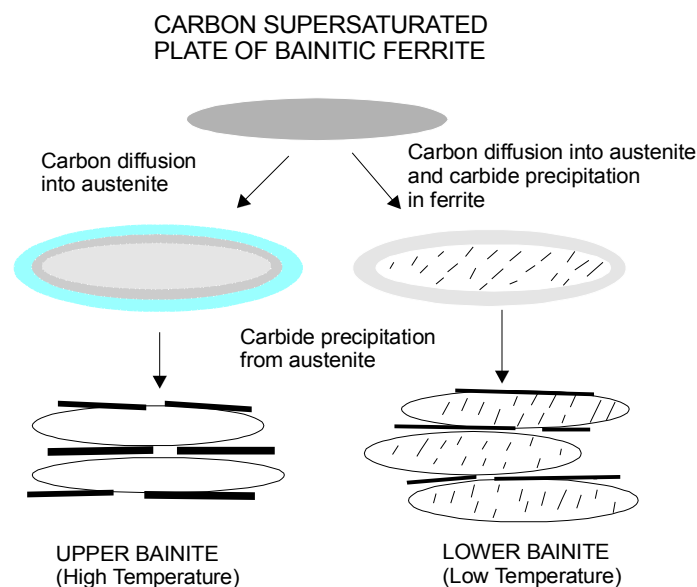


Fig. 2. Schematic illustration of the transition from upper to lower bainite [49]

The transition temperature is defined as the highest temperature at which time required to decarburise ferrite lath is smaller than the time necessary to obtain chosen volume fraction of cementite precipitation.

Table 1 is a summary of essential characteristics of the bainitic reaction according to the displacive mechanism in comparison to the main transformations that occur in steels.

The specific features of bainite transformation discussed above indicate that the mechanism of bainite transformation in steels has not yet been established despite much work both experimentally and theoretically. Today two completely different models, i.e. the diffusional and the displacive mechanism have been proposed [1, 2, 11, 19, 26, 66-71].

The diffusional school proposes that the ferritic component of bainite develops by a diffusional ledge mechanism. On the other hand the displacive school claims that the bainite

transformation occurs diffusionlessly as far as the solvent and substitutional solute atoms are concerned.

Table 1. Transformation characteristics for bainite α_b , Widmanstätten ferrite α_w , and martensite α' [2, 5]

	α'	α_b	α_w
Nucleation and growth reaction	√	√	√
Plate shape	√	√	√
Diffusionless nucleation	√	x	x
Carbon diffusion during nucleation	x	√	√
Substitutional diffusion during nucleation	x	x	x
Confined to austenite grains	√	√	√
Large shear	√	√	√
Invariant plane strain shape deformation	√	√	√
Diffusionless growth	√	√	x
Carbon diffusion during growth	x	x	√
Substitutional diffusion during growth	x	x	x
Glissile interface	√	√	√

Consistency of a comment with the transformation concerned is indicated by (√), inconsistency by (x).

In an attempt to obtain new information regarding the formation of bainite the present authors have decided to discuss thoroughly the selected controversies concerning the bainite transformation in the light of some their research work devoted bainite reaction. One basic controversy concerns the diffusive or displacive mechanism of bainite transformation; another the role of diffusion of carbon, and third controversy is connected to the question of the carbon content of the bainitic ferrite when first formed [1, 2, 72-80].

DIFFUSIVE OR DISPLACIVE MECHANISM OF BAINITE TRANSFORMATION

Although many of the characteristics of bainite especially the morphology and the shape deformation had been found to be similar to those of martensite a different microstructural approach was developed by Aaronson in 1962 [57]. He used the Dubè morphological classification [81] for all non-pearlitic forms of ferrite formed from austenite, and he attributed the morphological variations to the dependence of the growth kinetics of an interface, and to the nature of the site from which a precipitate crystal develops. In particular plate morphologies were regarded as the result of the formation of immobile partly coherent, planar interfaces which can grow normal to themselves only by the lateral migration of “ledges”. In later discussion of bainite Aaronson [58, 60] developed the “microstructural” definition in which bainite is regarded simply as non-lamellar two-phase aggregate of ferrite and carbides in which the phases form consecutively (as distinct from pearlite where they form co-operatively). Aaronson stated that according to this definition the upper limiting temperature of bainite formation should be that of the eutectoidal reaction (Ae_1) and he denied that the kinetic B_S temperature has any fundamental significance. In those alloy systems where there seems clear evidence for a separate C – curve for bainite, the bainitic “bay” and the apparent upper limit of bainite transformation (B_S) were

attributed to a special effect of certain alloying elements on the growth kinetics (solute drag-like effect – SDLE) [82]. Aaronson equally dismissed the observation on surface relief as a basis for classifying the various forms of ferrite.

Indeed, TTT diagrams of plain C steel exhibit a single C curve and some high alloy steels have two C curves [83]. The two C curves may result from a change with temperature in the mechanism of ferrite formation [82]. The change in mechanism with decreasing reaction temperature occurs at a characteristic temperature designated as the bay temperature T_b (Fig. 3). This is the temperature at which the two C- curves for initiation of transformation intersect. The bay temperature has also been called the bainite start temperature, B_s and its occurrence is attributed to SDLE [82].

If the mechanism of bainite transformation is assumed to be displacive bainite should have its own C curve [84-88]. On the other hand if both pearlitic and bainitic transformations occur in the same diffusional mechanism they should be involved in one C curve. In the latter case the apparent separation into two C curves will be given by the retardation of the transformation due to the solute-drag like effects (SDLE) [15-21]. In the case of the Cr and Mo steel the transformation diagram is separated into two distinct C curves (Fig. 3a) and it can be explained in terms of both diffusional and displacive theories.

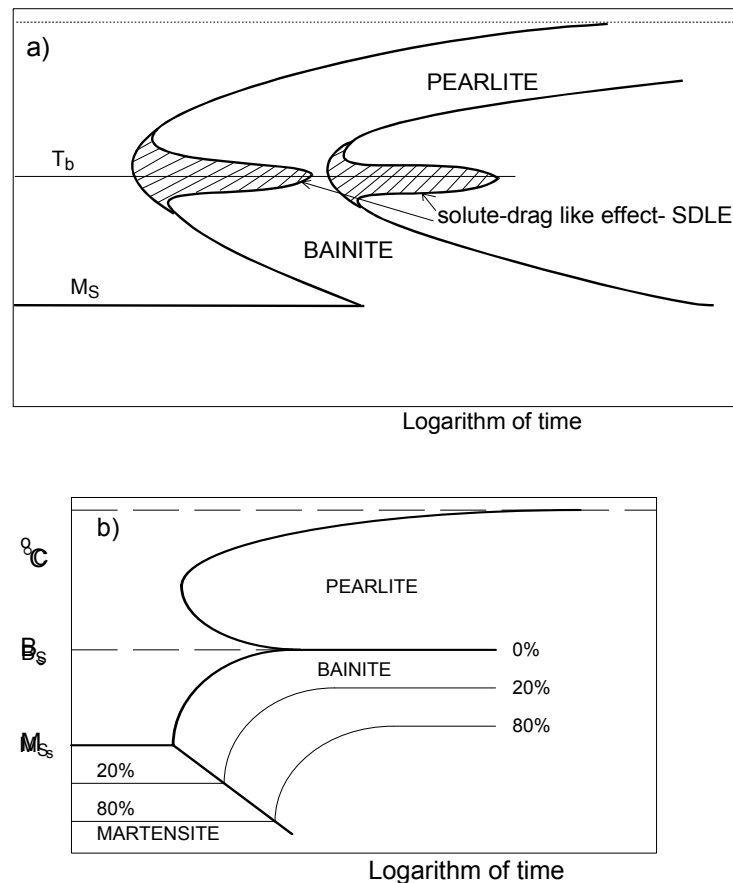


Fig. 3. Schematic representation of TTT diagrams expected by the diffusional and the displacive theories.
 a) the diffusional model with SDL effect, b) displacive model with two different C-curves

The SDLE was originally proposed by Kinsman and Aaronson [17, 18, 44] to explain sluggish ferrite growth kinetics in steels containing specific alloying elements.

On the SDLE hypothesis nonequilibrium absorption of a substitutional alloying element occurs to ferrite/austenite boundaries. When the element is one that reduces the activity of C, the effective C concentration gradient in austenite ahead of a growing ferrite crystal is reduced. Since this gradient is responsible for driving ferrite growth absorption of the solute element reduces ferrite growth kinetics. In extreme cases ferrite growth ceases altogether.

Transformation stasis (also called incomplete reaction phenomenon) [19, 89] can be explained by considering the influence of the SDLE upon ferrite growth together with the change in the mechanism of ferrite nucleation at the bay temperature [19]. At temperatures below T_b ferrite growth is greatly restricted by the SDLE. Transformation proceeds by the nucleation of a ferrite crystal on a pre-existing ferrite grain (sympathetic nucleation [19]), followed by a limited amount of growth. Once the SDLE inhibits the growth of the sympathetically nucleated crystal a new ferrite crystal nucleates and grows until the SDLE inhibits migration of its boundaries. However since ferrite growth is accompanied by C partitioning the driving force for sympathetic nucleation rapidly declines with the amount of ferrite formed. Transformation stasis begins when there is no longer sufficient driving force to support sympathetic nucleation of ferrite. Transformation does not resume until carbides form and the driving force for ferrite nucleation and growth is restored [17-19].

For the recent model for the SDLE [19] a solute drag like effect results when the chemical potential of C in the ferrite/austenite boundary is significantly less than the paraequilibrium value. Elements capable of reducing the C activity should produce an SDLE [60, 61, 82]. The elements Mo, Mn, Cr, V, Ti whose interaction parameters with C are negative should thus produce an SDLE and Ni and Si whose interaction parameters are positive should not.

However, a quantitative SDLE theory is unavailable and direct test of the hypothesis has not been done.

There are a number of difficulties with these concepts of SDLE. The basic concept of the "solute drag-like" effect [13-21, 54-62] is seems wrong. The suggested [13-21] reduction in the activity of carbon in the austenite should in fact lead to an increase in the concentration of carbon in the austenite near the interface, if the partial molar free energy of the carbon is to be the same in all phases [90]. The suggestion [21] that a species X which is segregated into the interface has an effect on the activity of carbon in adjacent austenite is itself doubtful [35, 91-93]. Even though the concentration of X in the interface may be different from that in the bulk of austenite its influence on the activity of C in austenite will be identical to that of the X atoms in the bulk of austenite [35]. The suggestion [13-21] that bays in TTT curves arise due to "solute drag-like" effects is also inconsistent with experimental evidence; such bays can also be found in steels where the alloying elements raise the activity of carbon in austenite [25]. For example the Fe-Mn-Si-C alloy [25] has a larger activity coefficient for carbon in austenite than plain carbon steel but this alloy exhibits a bay in its TTT diagram.

A possibility to test the diffusive hypothesis against the displacive one is to check the effect of alloying elements. If there are random jumps of the lattice atoms across the moving α/γ interface then there should also be some diffusion of substitutional elements relative to each other and that should result in a solute drag. Alloying elements would then decrease the growth rate of bainite more than according to so-called paraequilibrium [66].

However reconstructive transformation with local equilibrium requires some perturbation of the substitutional solute content in the proximity of the interface. Very detailed atom-probe experiments, which have a chemical and spatial resolution on an atomic scale, have failed to show any evidence of such redistribution of alloying elements (Cr, Mn, Mo, Ni and Si) at the interface between bainitic ferrite and austenite [94-97].

Finally it should be noted that despite much work on bainite made by many investigators there is no convincing evidence for the existence of superledges in the bainite/austenite interface. The superledges thus remain hypothetical in the model for bainite growth by a diffusional mechanism [11, 40].

In any case the superledge mechanism does not explain the plate morphology of bainite. Allotriomorphic ferrite which grows diffusionally often exhibits systematic and very convincing arrays of growth ledges in the transformation interface and yet does not have a plate morphology. The suggestion [61, 64] that changes in acicularity can be understood in terms of variations in the relative migration rates of disordered and ledged boundaries as a function of temperature is incorrect because allotriomorphic ferrite does not assume a plate shape at any temperature.

Furthermore, the evidence of Whiting [62], Hsu et al. [98] and Nemoto [99] on the existence of ledges is not convincing because of the poor resolution and because the observations do not show any ledges, consisting of planar facets, which are then displaced by the movement of steps. It should be pointed out that whether the interface is displaced continuously or by a step mechanism has little relevance to the mechanism of transformation; both mechanisms of interface displacement can be consistent with diffusional or displacive transformation [100-103].

It is difficult to accept the attempt at explaining why allotriomorphic ferrite, which can grow by a ledge mechanism, does not develop into a plate shape; both Widmanstätten ferrite and allotriomorphic ferrite can grow from austenite grain boundaries, but only the former develops into a plate shape [104, 105].

THE ROLE OF CARBON DIFFUSION

It is simple to establish that martensitic transformation is diffusionless, by measuring the local compositions before and after transformation. Bainite forms at somewhat higher temperatures where the carbon can escape out of the plate within a fraction of a second. Its original composition cannot therefore be measured directly.

There are indeed three possibilities. The carbon may partition during growth so that the ferrite may never contain any excess carbon. The growth may on the other hand be diffusionless with carbon being trapped by the advancing interface. Finally, there is an intermediate case in which some carbon may diffuse with the remainder being trapped to leave the ferrite partially supersaturated [13, 21, 61, 82, 106]. It is therefore much more difficult to determine the precise role of carbon during the growth of bainitic ferrite than in martensite. Diffusionless growth requires that transformation occurs at a temperature below T_0 , when the free energy of bainite becomes less than that of austenite of the same composition. A locus of the T_0 temperature as a function of the carbon concentration is called the T_0 curve, an example of which is plotted on the Fe-C phase diagram in Fig. 4. Growth without diffusion can only occur if the carbon concentration of the austenite lies below of the T_0 curve [107-109]. Diffusionless transformation is thermodynamically impossible if the carbon concentration of the austenite exceeds the T_0 curve* (exactly speaking it corresponds to the x_{T_0} carbon concentration on the phase diagram). These conclusions are not significantly modified when the strain energy of transformation is included in the analysis.

From a fundamental point of view the interesting question is what kind of equilibrium governs the conditions at the $\alpha/\alpha+\gamma$ interface. We should thus distinguish between two cases:

* The T_0 temperature on the Fe-C phase diagram corresponds to the x_{T_0} carbon concentration and T_0' temperature is related to x_{T_0}' that is the carbon concentration with allowing for 400 J/mol of stored energy in the ferrite in order to make calculations for bainitic ferrite.

1. local equilibrium for interstitials only,
2. diffusionless, i.e. no local equilibrium, (the third case of full local equilibrium for lattice atoms and for interstitials should be excluded).

However it should be emphasised that there is a whole series of cases intermediate between cases (1) and (2) which also are without local equilibrium.

The role of carbon in the growth of bainite is difficult to resolve directly. The relatively high temperatures where bainite typically forms provide an opportunity for the excess of carbon to diffuse rapidly into residual austenite before any experimental measurements can be made [110, 111].

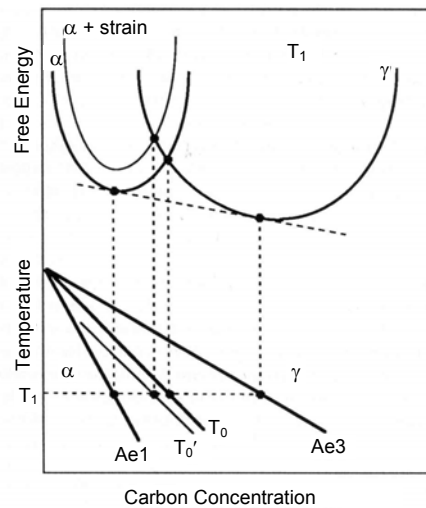


Fig. 4. Schematic illustration of the origin of the T_0 construction on the Fe-C phase diagram. The T_0' curve incorporates a strain energy term for the ferrite, illustrated on the diagram by raising the free energy curve for ferrite by an appropriate quantity

Let suppose that the plate of bainite forms without diffusion, but any excess carbon is soon rejected into the residual austenite. The next plate of bainite then has to grow from carbon-enriched austenite (Fig. 5). This process must cease when the austenite carbon concentration reaches the T_0' curve. The reaction is said to be incomplete, since the austenite has not achieved its equilibrium composition (given by the Ae_3 curve) at the point the reaction stops. If on the other hand, the ferrite grows with an equilibrium carbon concentration then the transformation should cease when the austenite carbon concentration reaches the Ae_3 curve [39, 107, 112, 113].

There are two important features of bainite which can be shown by a variety of techniques, e.g. dilatometry, electrical resistivity, magnetic measurements and by metallography. Firstly, there is a well-defined temperature B_S above which no bainite will form, which has been confirmed for a wide range of alloy steels. The amount of bainite that forms increases as the transformation temperature is reduced below the B_S temperature. The fraction increases during isothermal transformation, as a sigmoidal function of time, reaching an asymptotic limit, which does not change on prolonged heat treatment even when substantial quantities of austenite remain untransformed. Transformation in fact ceases before the austenite achieves its equilibrium composition, so that the effect is called the "incomplete-reaction phenomenon". These observations are understood when it is realised that growth must cease if the carbon concentration in the austenite reaches the T_0' curve of the phase diagram. Since this condition is

met at ever increasing carbon concentrations when the transformation temperature is reduced, more bainite can form with greater undercoolings below B_S . But the T_0 restriction means that equilibrium, when the austenite has a composition given by the Ae_3 phase boundary, can never be reached, as observed experimentally.

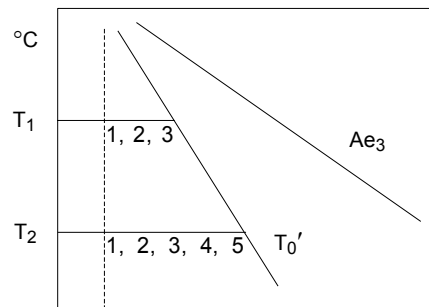


Fig. 5. Illustration of the incomplete reaction phenomenon. During isothermal transformation, a plate of bainite grows without diffusion and after this event excess of carbon is partitioned into the residual austenite. It means that the partitioning of carbon into the residual austenite occurs subsequent to transformation of subunits of bainitic ferrite. The next plate therefore has to grow from carbon-enriched austenite (it starts from the bulk carbon concentration \bar{x} and passes through points 1,2,... 5)

It is usually assumed that the point where dimensions cease to change represents full transformation. But in case of bainitic transformation, reaction ceases before the parent phase has completely transformed. It means that at any temperature below B_S and in the absence of any interfering secondary reactions only a limited quantity of bainitic ferrite forms before the reaction terminates. It is found experimentally that the transformation to bainite does indeed stop at the T_0' boundary (Fig. 6a and b)*.

The carbon concentration of the residual austenite increases during bainitic transformation as a consequence of the increasing volume fraction of bainitic ferrite (Fig. 6). Given that the excess carbon in the bainite ferrite partitions into the residual austenite and assuming that the final microstructure consists of only bainitic ferrite and residual austenite it is possible to estimate the carbon concentration in residual austenite.

The determined carbon concentrations of the residual austenite at the point where the formation of bainite ceases are compared with the T_0 , T_0' and $A'e_3$ phase boundaries for investigated steels (35HGS and 15HM2VT) in Figure 6. The diagrams were calculated as in Ref. [39, 107] using a model developed by Bhadeshia [11, 22, 26, 84] based on the McLellan and Dunn quasi-chemical thermodynamic model [114-117]. The T_0' curve allows for 400 J/mol of stored energy in the bainitic ferrite to take account of the strain energy due to the invariant-plane strain shape change that accompanies the growth of bainitic ferrite [11, 84]. The $A'e_3$ curve is the calculated paraequilibrium $(\alpha + \gamma)/\gamma$ phase boundary indicating equilibrium between ferrite and austenite when the ratio of substitutional alloying elements to iron is constant everywhere. The bainite and martensite reactions start temperatures B_S and M_S are also marked on these diagrams. The paraequilibrium phase boundary is chosen because no substitutional alloying element partitioning occurs during bainite formation. In presented diagrams the reaction is found to stop when the average carbon concentration of the residual austenite is close to the T_0' curve

* In Fig. 6 the reaction seems to stop between the T_0 and T_0' lines. This might be explained by the fact that the T_0' line accounts for 400 J/mol of stored energy in the bainite. If this energy is reduced by plastic deformation of the surrounding austenite then a higher volume fraction of bainite should be able to form.

than the $A'e_3$ boundary (black circles in Fig. 6). The presented above results can be explained when it is assumed that bainitic ferrite grows without diffusion, but any excess of carbon is soon afterwards rejected into the residual austenite by diffusion [11]. This makes more difficult for subsequent bainitic ferrite to grow, when the austenite becomes stabilised by increased carbon concentration. The maximum extent to which the bainite reaction can proceed is therefore determined by the composition of the residual austenite. A stage where diffusionless growth becomes thermodynamically impossible and the formation of bainitic ferrite terminates is where the carbon concentration of the austenite reaches the T_0' curve. Thus, the incomplete reaction phenomenon supports the hypothesis that the growth of bainitic ferrite occurs without any diffusion with carbon being partitioned subsequently into the residual austenite.

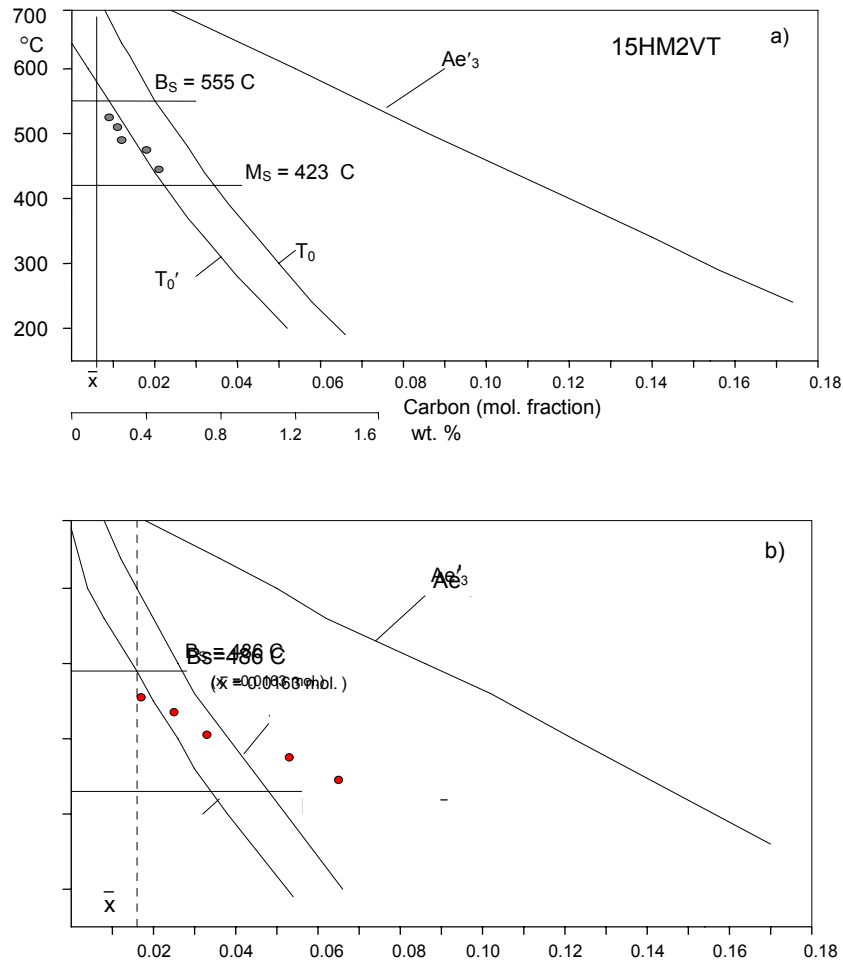


Fig. 6. Calculated phase diagram with experimental data of carbon concentration of residual austenite at the termination of isothermal bainite formation for: a) 15HM2VT steel (black circles represent experimental data) [108, 109], b) 35HGS steel [86, 87]

The analysis suggests that bainite grows by displacive transformation but carbon atoms partition into the residual austenite (or precipitate as carbides), shortly after growth is arrested. The precipitation of carbides is therefore a secondary event.

The bainitic ferrite forms as a metastable ferrite and the redistribution of carbon atoms mainly occurs after the formation of ferrite. The increase in carbon concentration of retained austenite with the bainite reaction time has been already reported in silicon containing steels by Matas and Hehemann [52] and Bhadeshia and Waugh [118].

The residual austenite that has left after transformation to bainite, exhibits two basic morphologies, *i.e.* film austenite which is retained between the subunits within a given sheaf of bainite and “blocky austenite” which is bounded by different bainite sheaves. The distribution of carbon in those two forms of the residual austenite is not homogeneous after continuous cooling or isothermal transformation to bainite. The austenite is enriched to a greater extent in the regions trapped between the platelets [52, 119] than the blocky austenite [118]. Matas and Hehemann [52] and Ławrynowicz [119] (Fig. 7) proved the existence of non-uniform distribution of carbon in the austenite retained after bainitic transformation, using a X-ray diffraction technique and dilatometry analysis respectively.

It is found that in samples partially transformed to bainite during subsequent quenching to ambient temperature can be registered two martensite start (M_S) temperatures. Because M_S temperature depends directly on a carbon content in austenite, the obtained results may indicate that the carbon concentration trapped in films of austenite between parallel subunits of bainitic ferrite is much larger than in the blocks of austenite. It would point out to a necessity of a substantial modification of bainite and martensite regions on the TTT (CCT) diagrams.

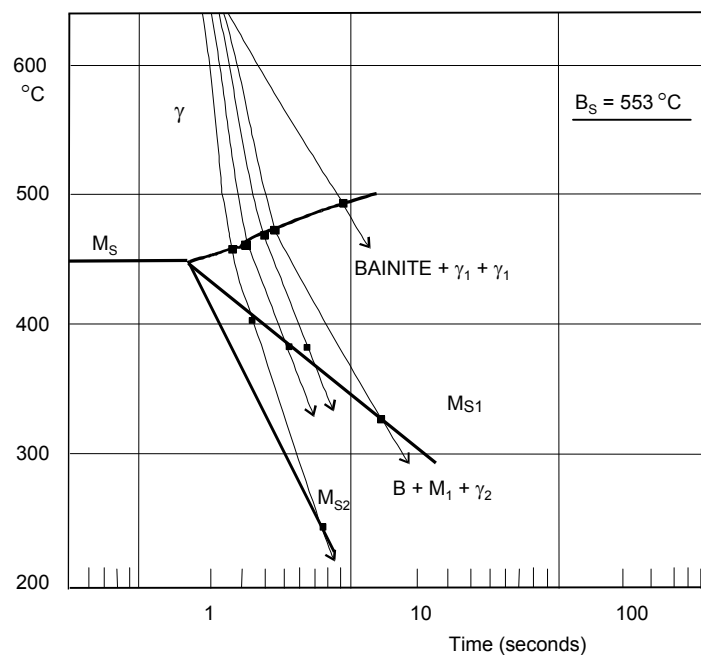


Fig. 7. Dilatometrically determined onset of the bainite and martensite reaction in 15HM2VT steel during continuous cooling (CCT curve) [119]

SURFACE RELIEF CAUSED BY BAINITIC TRANSFORMATION

As pointed out by Christian [6, 9, 40] a planar interface traversing a crystal and having no long range elastic field produces an invariant plane strain (IPS) shape change for all transformations. However when the IPS shape change has a large shear component (Fig. 8) it implies the coherency at the interface parent/product which must be glissile.

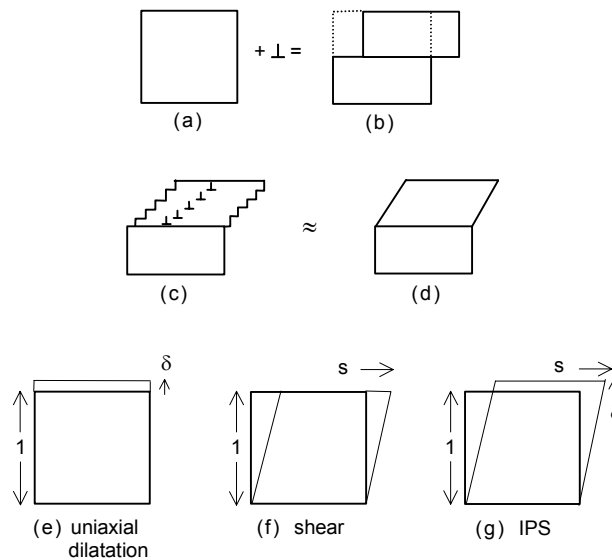


Fig. 8. (a, b) Step caused by the passage of a slip dislocation. (c, d) Many slip dislocations, causing a macroscopic shear. (e) An invariant-plane strain with a uniaxial dilatation. (f) An invariant-plane strain which is a simple shear. (g) An invariant-plane strain which is the combined effect of a uniaxial dilatational strain δ and a simple shear s . Dilatational strain, is directed normal to habit plane [40]

The phenomenological theory of martensite crystallography solves the problem for the $\text{fcc} \rightarrow \text{bcc}$ transformation with the observed shape deformation which leaves the habit plane undistorted and unrotated (IPS – it is an invariant-plane strain). (Fig. 9).

The Bain strain (B) converts the structure of the parent phase into that of the product phase. When combined with an appropriate rigid body rotation (R), the net homogeneous lattice deformation RB is an invariant-line strain (step a to c in Fig. 9). However, the observed shape deformation is an invariant-plane strain $P1$ (step a to b in Fig. 9), but this gives the wrong crystal structure. If a second homogeneous shear $P2$ is combined with $P1$ (step b to c), then the correct structure is obtained but the wrong shape since

$$P1 P2 = RB$$

These discrepancies are all resolved if the shape changing effect of $P2$ is cancelled macroscopically by an inhomogeneous lattice-invariant deformation, which may be slip or twinning as illustrated in Fig. 9.

The theory explains all the observed features of the martensite crystallography. The orientation relationship is predicted by deducing the rotation needed to change the Bain strain into an

invariant-line strain. The habit plane does not have rational indices because the amount of lattice-invariant deformation needed to recover the correct the macroscopic shape is not usually rational. The theory predicts a substructure in plates of martensite (either twins or slip steps) as is observed experimentally. The transformation goes to all the trouble of ensuring that the shape deformation is macroscopically an invariant-plane strain because this reduces the strain energy when compared with the case where the shape deformation might be an invariant-line strain.

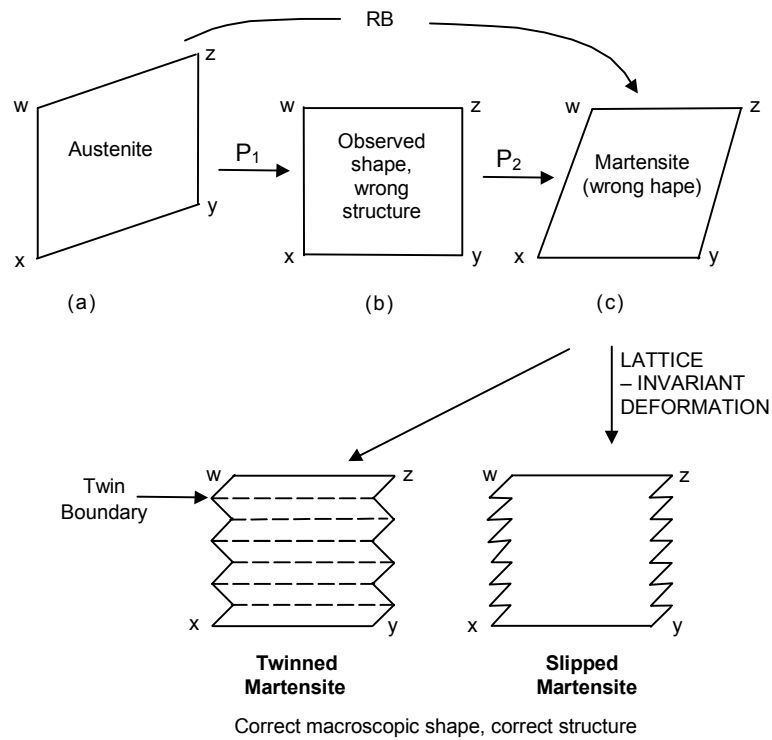


Fig. 9. The phenomenological theory of martensite crystallography [2, 5, 40]

Another implication of an IPS shape deformation is that the product phase must be in the form of a thin plate whose habit plane is the invariant plane [40]. This is because the strain energy due to the IPS shape deformation is then minimised [120, 121]. It is not therefore surprising that in all instances where austenite transforms to plate shaped ferrite the growth of the ferrite causes an IPS shape change (Table 2). This is not the case when the ferrite grows in any other shape.

Table 2. Approximate values of s and δ for variety of transformation products in steels [120]

Transformation	s	δ	Morphology	Ref.
Widmanstätten ferrite	0.36	0.03	Thin plates	122, 123
Bainite	0.22	0.03	Thin plates	2, 122, 123
Martensite	0.24	0.03	Thin plates	123

Of the transformation products listed in Table 2 both Widmanstätten ferrite and martensite can be obtained in the form of plates which can be observed using an optical microscope.

However the microstructure of bainite consists of fine plates of ferrite each of which is only 0.2 μm in thickness which is below the limit of light microscopy. These plates are called “subunits” because they grow in clusters known as sheaves. Within each sheaf the subunits are parallel and of identical crystallographic orientation and habit plane. The subunits are usually separated from each other either by the presence of carbides or residual austenite [2, 40].

This fine microstructure has made it difficult to establish the surface relief introduced as bainite grows. Ko and Cottrells’ classic work [36] qualitatively established the nature of the surface relief. Subsequent light microscopy [30, 31, 123] indicated values of $s \sim 0.13$ which were found to be inconsistent with the larger values predicted by theory which are in the range 0.22–0.28 [31, 37]. These difficulties are associated with the fact that light microscopy can only reveal the average shape deformation of the whole sheaf rather than of an individual subunit. This was demonstrated by Sandvic [32, 67, 68] who determined from the displacement of twin boundaries by subunits using transmission electron microscopy that the value of s is close to 0.22 which is consistent with theory.

The formation of bainite causes a deformation (Fig. 10) which is an invariant-plane strain with a shear component of about 0.26 and a dilatational strain normal to the habit plane of about 0.03. This is consistent with a displacive mechanism of transformation. Bainite forms at a relatively high temperature when compared with martensite. The parent austenite is weaker at high temperatures and cannot accommodate the large shape deformation elastically. It therefore relaxes by plastic deformation in the region adjacent to the bainite. The plastic accommodation of the shape strain is mostly confined to the austenite as would be expected theoretically [6, 9, 40]. This is evident in Fig. 10c, d. The effect of this plastic deformation is to stifle the growth of bainite plates before they hit any obstacle. This is why each bainite plate grows to a size which is often smaller than the austenite grain size and then comes to a halt. Further transformation happens by the formation of a new plate and this is why the sheaf morphology arises.

The work shows that the shape strain is in fact larger than was reported in earlier work [30, 31]. This is because the early data were derived using light microscopy in which case they refer to the shape deformation averaged over a sheaf rather than to an individual subunit. The results indicate that the maximum value of the shear strain is about 0.26. This is consistent with the phenomenological theory of martensite crystallography. The shape change is not elastically accommodated but there is significant plastic deformation caused in the adjacent austenite.

It has been proposed that IPS surface relief effect of the type associated with martensitic transformations arises even during a diffusional transformations, simply due to the existence of a sessile semi-coherent or coherent interface which is displaced by the movement of “disordered ledges” [54-62, 124-126]. The ledges themselves are considered to have an incoherent structure. We believe that this proposal is incorrect. The existence of an IPS relief implies co-ordinated movements of atoms inconsistent with the concept of a diffusional transformation and with the structure of the incoherent ledge whose motion leads to transformation. Christian and Edmonds [11, 40] have shown that the proposal also implies the existence of an atomic correspondence across just the sessile part of the interface and this is an impossible concept since atomic correspondence is a property of the particle as a whole.

The second main point of controversy concerns factors determining the morphology of precipitates in steels. The shape change accompanying the formation of Widmanstätten ferrite and bainite in steels is known to be an IPS with a large shear component [120, 122, 123]. The strain energy due to this shape deformation causes the plates to adopt thin plate morphology

[127-131]. Aaronson and co-workers have ignored the influence of shape change on morphology and instead claim that the plate morphology is a consequence of variation of interface mobility as a function of interface orientation. Their ideas do not explain the lack of plate morphology in the case of allotriomorphic ferrite which grows diffusively but which can otherwise be similar to Widmanstätten ferrite [2, 40, 69].

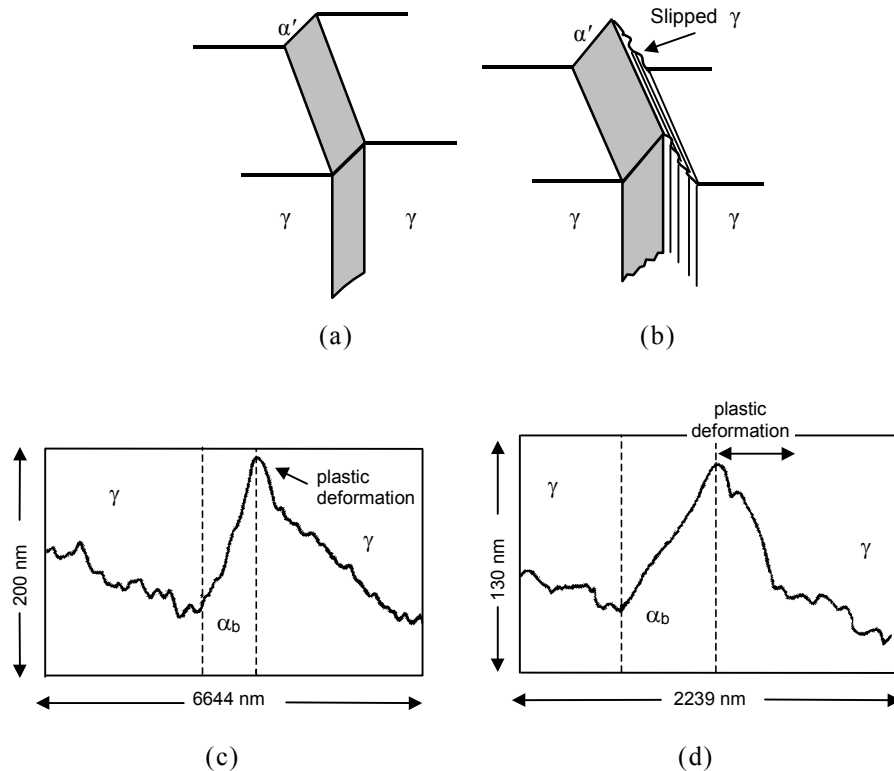


Fig. 10. (a) A perfect invariant-plane strain surface relief effects. (b) One where plastic relaxation of the shape change occurs in the adjacent matrix. (c, d) An actual atomic force microscope scan across the surface relief due to a bainite sub-unit [120]

THICKENING PROCESS OF BAINITIC FERRITE LATHS

For clarifying the transformation mechanism it is of great importance to examine the thickening process beside the carbon concentration of bainitic ferrite.

If bainitic ferrite forms by the diffusional mechanism with a local equilibrium condition it has the carbon concentration in equilibrium with respect to austenite. Moreover it can grow until the average carbon concentration of the untransformed austenite reaches the equilibrium value with respect to ferrite, if the so-called “solute drag-like effect” [1, 54-61] is absent.

On the other hand if bainitic ferrite develops by a displacive mechanism, the carbon concentration of it can be higher than the equilibrium value with respect to austenite. Moreover, it may not thicken after growing to a limited size due to a loss of coherency of the interface boundaries [132, 133].

The measurements of the thickening process and carbon concentration of bainitic ferrite are usually difficult for the bainite transformation of conventional carbon steels because of the rapid precipitation of carbides and the absence of untransformed austenite within a bainitic packet or sheaf. However, it is now well known that in the carbon steels containing about 2% silicon carbide-free, lath-shaped, bainitic ferrite forms and is separated one from another by carbon-enriched retained austenite in early stages of transformation [134, 135].

Moreover, because bainitic ferrite laths in a packet are in contact with austenite [136-138] we can examine the thickening of bainitic ferrite by measuring the change in lath width distribution with the reaction time. In silicon containing alloys the solute drag-like effect is not necessary to be taken into consideration, because silicon increases carbon activity in austenite.

If the bainitic ferrite develops by the diffusional mechanism with a local equilibrium condition it could grow until the average carbon concentration of the untransformed austenite reaches the paraequilibrium value because the solute drag-like effect is not expected in the silicon-containing alloy. However the primary ferrite did not thicken during the subsequent isothermal holding (Fig. 11). This result suggests that the bainitic ferrite forms by a displacive mechanism with the glissile movement of coherent interface boundary and thus the growth of it is limited by the loss of coherency of the interface boundary.

This suggests that the interface had already lost its mobility as a glissile interface. Because of high reaction temperatures the interfacial structure may change by a diffusional mode after stopping the glissile movement in order to release the strain energy caused by a shear as was suggested by Bhadeshia [22, 25].

The results for the thickening process of bainitic ferrite are contrary to the diffusional ledge mechanism with a local equilibrium condition and strongly indicate that the bainitic ferrite develops by a displacive mode.

MODELLING OF ADVANCED BAINITIC STEELS

It is well established that in many steels, especially those with large concentrations of silicon or aluminium carbide precipitation reaction lag far behind the growth of bainitic ferrite [139-142]. As a consequence the carbon which is rejected from the bainitic ferrite enriches the residual austenite thereby stabilising it to martensitic transformation during cooling to ambient temperatures. The mixture of bainitic ferrite and austenite is in principle an ideal combination from many points of view. This two phase microstructure derives its strength from the ultrafine grain size giving an effective grain size which is much less than 1 μm . Such a small grain size cannot be achieved by any commercial process other than mechanical alloying (powder metallurgical process). A fine grain structure is an optimum method for improving strength since unlike most other strengthening mechanisms the improvement in strength is also accompanied by an improvement in toughness. The dispersed and ductile austenite films between the ferrite platelets can be expected to have a crack blunting effect. All this benefits can be achieved by creating a duplex microstructure with the cheapest austenite stabiliser available, carbon, which concentration in the austenite is enhanced during transformation so that the average carbon concentration of the steel need not be large.

In spite of all these advantages the bainitic ferrite-austenite microstructure has failed to live up its promise, primarily because of the instability of relatively large or blocky regions of austenite, which become trapped between sheaves of bainite. The blocks of austenite tend to transform to high carbon untempered martensite under the influence of small stresses and consequently have an embrittling effect. The films of austenite that are trapped between the platelets of ferrite in a sheaf are much more stable partly because of their higher carbon concentration but also because of the constrain to transformation from the surrounding plates of ferrite.

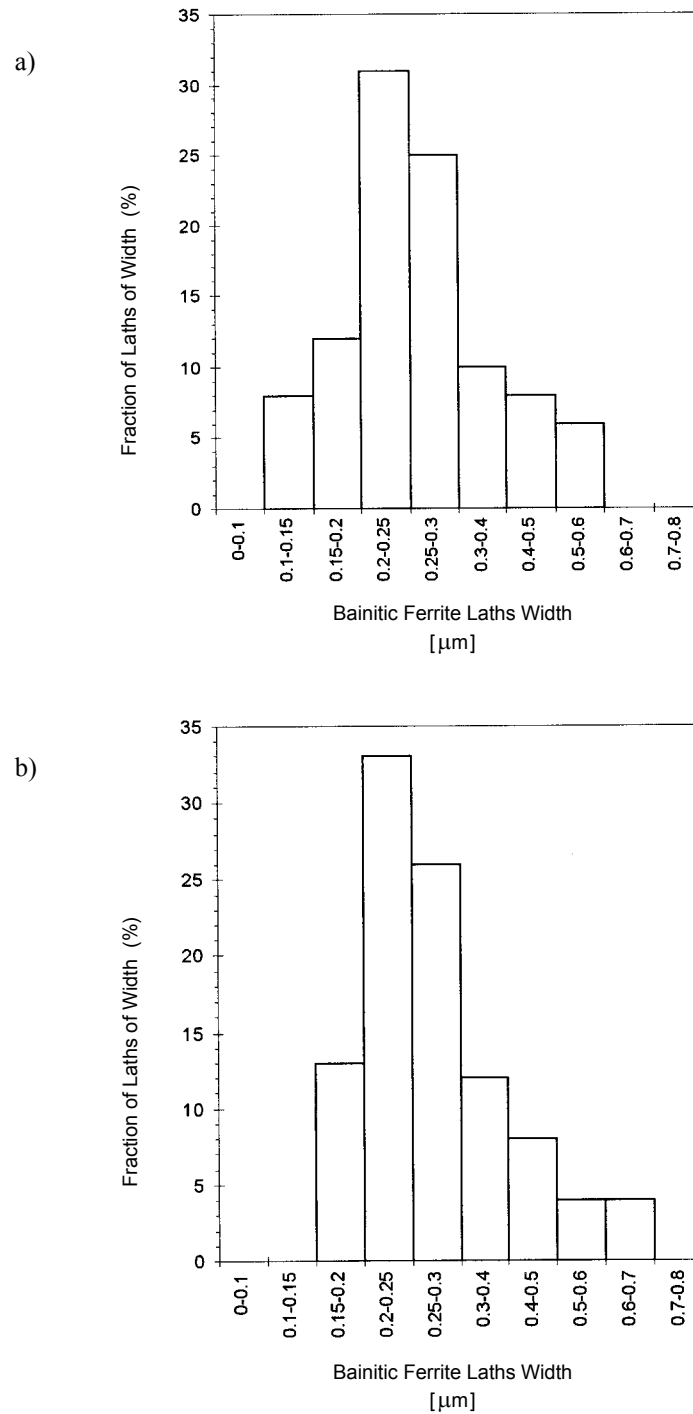


Fig.11. Distribution of the lath widths of the bainitic ferrite in 35HGS steel for different isothermal holding times at temperature 350°C, a) 5 minutes, b) 60 minutes. The width of bainitic ferrite laths were obtained with TEM micrographs where broad face boundaries of the laths were close to edge-on [112]

It is found experimentally that high strength and good toughness can be obtained by maintaining the ratio of the volume fractions of the films of austenite to blocky austenite to a value greater than 0.9 [143, 144]. The question then arises as to the factors, which control this ratio. Therefore every effort has to be made to reduce the fraction of blocky austenite present in the microstructure and increase its stability to martensitic transformation. The aim of alloy design should then be to increase the maximum permitted degree of transformation to bainitic ferrite. There are in fact four different ways of minimising the volume fraction of blocky austenite, each involving an increase in the volume fraction of bainite:

1. Increasing in the extent of reaction by altering the transformation time, however in the later stages of transformation the possibility of carbide precipitation arises,
2. Lowering the transformation temperature permits the bainite reaction to proceed to a larger extent but there is a limit to the minimum transformation temperature since the lower bainite and martensite reactions eventually set in. The best mechanical properties is observed when the retained austenite is present mainly in the form of films between the sub-units of bainite, rather than as blocky regions between the sheaves of bainite [143]. Hence the optimum retained austenite content increases as the transformation temperature decreases because the sub-unit thickness decreases permitting more of the austenite to be in the film morphology for a given volume fraction of transformation to bainite.
3. An increase in the extent of reaction can also be achieved by reducing the overall carbon concentration of the steel so that the austenite reaches its limiting composition at a later stage of the reaction.
4. The T_0' curves of the phase diagram which determine the composition of the austenite at the point where the reaction stops can also be shifted to higher carbon concentration by altering the substitutional solute concentration of the steel (Fig. 12) [145]. The T_0' concept can be used to optimise the mechanical properties by minimising blocky, unstable austenite [146]. An increase in the amount of bainitic ferrite in the microstructure is needed in order to consume the blocks of austenite. The level of alloying additions has to be kept low enough to avoid the formation of martensite.

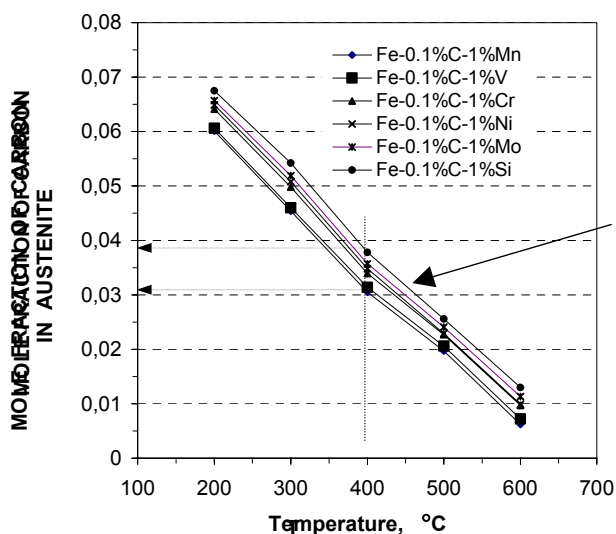


Fig. 12. Calculated T_0' curves for Fe-0.1C-X steels (where X means different kind of substitutional alloy elements such as: Mn, V, Cr, Ni, Mo and Si). Note that substitution 1%V with 1%Si shifts the T_0' to higher carbon concentration in austenite with about 20% [145]

Typical compositions of the high strength steels, which show good toughness, are given in Table 3.

These three new alloys have been proposed as new high strength bainitic steels. The theoretical design of their composition has been made through the knowledge of phase transformation theory. The alloys listed in Table 3 have been proposed following a very large number of theoretical investigations.

Table 3. *Chemical composition of alloys designed, wt-% [146]*

Alloy	C	Si	Mn	Ni	Cr	Mo	V
Mn	0.30	1.5	2.00	–	1.30	0.25	0.1
Ni1	0.30	1.5	–	3.5	1.44	0.25	0.1
Ni2	0.30	1.5	–	3.5	1.44	0.25	–

In order to increase the maximum volume fraction of bainite in the final microstructure and to improve hardenability the following modifications of chemical compositions were proposed:

1. To suppress carbide precipitation the silicon content was reduced to the required minimum, 1.5 wt-% Si.
2. It was found that the T_0' curve shifts to higher carbon when the Mn content is reduced. Then, with the aim of increasing the strength of the alloy the carbon content should be increased to 0.3 wt-%C with a reduction in the Mn content.
3. Improvements in the strength and hardenability were obtained by adding 1.44 wt-% Cr to the alloy.
4. An addition of 0.25 wt-% Mo was made to reduce impurity embrittlement. This addition shifted the T_0' curve to lower austenite carbon concentration and hence the molybdenum was limited to 0.25 wt-%.
5. In order to restrict austenite grain growth during the austenitization vanadium was added, 0.1 wt-%V.

Experimental data of mechanical properties of the designed steels are presented in Table 4 [147].

Table 4. *Tensile and fracture toughness properties [147]*

Alloy	YS MPa	UTS MPa	Elongation %	RA %	K_{max} MPa m ^{1/2}
Mn	1167	1790	13	44	–
Ni1	1150	1725	14	55	125
Ni2	1100	1625	14	59	128

YS – yield strength, UTS – ultimate tensile strength,

RA – reduction of area,

K_{max} – stress intensity factor at maximum load

Figure 13 shows the mechanical properties for quenched and tempered steels. It is evident that in some cases the properties match those obtained from much more expensive maraging steels. The carbide free bainitic steels are found to have the highest combination of strength and toughness for bainitic steels, matching even the maraging steels, which are about thirty times more expensive.

The mechanical property data on these high silicon steels designed using the phase transformation theory look extremely promising.

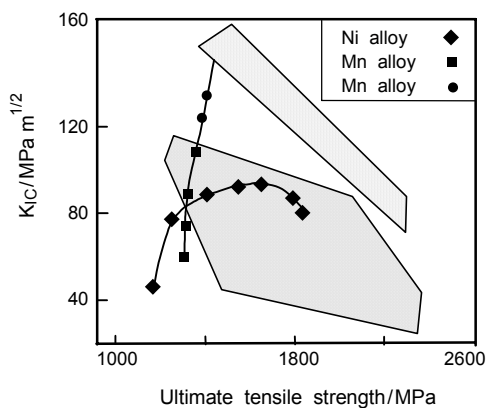


Fig. 13. New, cheap bainitic steels (points) which match properties of expensive alloys [148-150]

CONCLUSIONS

It is impossible in a short paper such as this, discuss the progress that has been made on the mechanism of the bainite transformation in steels. The references listed in this paper are much better reviews in this respect. There are still existing keen controversies concerning diffusive and displacive mechanisms of bainite transformation. The analysis suggests that bainite grows rather by displacive mechanism. The growth is accompanied by a shape change, which is an invariant-plane strain with a large shear component. Consistent with a vast array of experimental evidence the growth of bainite is supposed to be diffusionless, with the carbon partitioning into the residual austenite shortly after the growth of each bainite plate is stifled. This has the important consequence that transformation ceases as soon as diffusionless growth becomes thermodynamically impossible to sustain. As could be seen on the basis of displacive mechanism of transformation, the theory for the bainite transformation is at a sufficiently advanced stage to allow its use in the design of novel steels.

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