The Bainite Controversy

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Abstract

There has long existed a controversy regarding the formation of the bainite phase in steels. Nonetheless, following the clear identification of bainite in 1930, several characteristic features associated with the bainite transformation became well established. These features include: the classification into upper and lower bainite; the existence of a bainite-start temperature; and the incomplete-reaction phenomenon. Accordingly, two competing theories have been developed to explain the bainite transformation. However, no overriding consensus has been reached as to which is correct.

The first theory invokes a diffusion-controlled transformation, describing the growth of bainite via the propagation of 'ledges' — a series of steps on the transformation interface. The second interpretation favours a displacive, diffusionless transformation. Bainite growth occurs via the autocatalytic nucleation and growth of successive sub-units or platelets. Over time, a wealth of techniques has been implemented in order to increase the understanding of the mechanism by which bainite forms. From the early approaches that involved thermodynamic and kinetic considerations; through detailed work on the crystallography of the transformation; to studies involving advanced characterisation techniques that focused on the distribution of atoms, etc. Some of the theories have been progressively adapted to new evidence and new concepts as they emerge. For example: the concepts of the T_0 curve and of paraequilibrium transformation.

This work presents a chronological summary of the two theories of the bainite transformation, charting their progression and noting the variety of evidence both in support of and in contradiction to each viewpoint. The 'bainite controversy' is still debated by steel metallurgists today, although it has mostly been reduced to the question of whether or not bainitic ferrite initially forms with a supersaturation of carbon. This review gathers and evaluates some of the accumulated work in the hope that this question may finally be answered.

KEYWORDS: Steels; Bainite; Displacive models; Diffusive models; Phase transformations

1 Introduction

The value of a scientific theory lies both in its ability to explain our observations and in its usefulness as a predictive tool. A theory of phase transformations is no different in this regard, enabling us on the one hand to account for observed microstructural features and, on the other, to design new microstructures according to our own requirements.

Metallurgy is a strongly practical subject, driven by the development of new alloys with improved properties. The bainitic microstructure has become widely used in industrial applications and as technology evolves, greater demands are placed upon materials. It is thus essential to develop a quantitative understanding of the kinetics of the bainite transformation, so that new alloys may be designed to meet high performance industry standards. More ambitiously, one could create steels with better-than-expected properties, opening up the potential for new applications.

The progress towards a quantitative theory of the bainite transformation has been controversial, however, with opinion divided as to whether the mechanism is diffusion-controlled or displacive and diffusionless. This review is intended to chart the development of the two theories — from their initial conception to the quantitative models as they exist today.

To begin with, it is important to highlight that there have been many attempts to produce an exact definition of bainite, based upon microstructural or kinetic features. However, it has been difficult to settle on a generally accepted definition [1, 2, 3]. The various definitions can be inconsistent with each other, so a phase may be called bainite in terms of one definition but not another [1, 2, 3, 4, 5]. Although this is relatively inconsequential when simply describing a structure, problems arise when the definition is used to link the structure to a specific mechanism. Over time, some less familiar forms of bainite have been described: these include granular bainite [6], columnar bainite [7] and inverse bainite [8]. These terms have value in communicating the appearance of a microstructure. However it is misleading to imagine that the morphologies share similar, 'bainitic', mechanisms of transformation, since they do not [9].

Granular bainite is the most 'accurate' term of the three, commonly used to describe the (partly) bainitic

microstructure obtained from a continuous cooling process. The appearance is of a coarse ferrite matrix containing islands of martensite and austenite [6, 10], although in reality the ferrite region is made up of bainitic ferrite sheaves separated by thin regions of austenite [11]. The granular appearance is due to the gradual transformation that occurs during continuous cooling, resulting in the formation of coarse sheaves of bainite. On an optical scale, it looks different from 'ordinary' bainite; in the electron microscope, the two structures are similar [12]. Inverse bainite forms in hyper-eutectoid steel, with cementite precipitating first and ferrite forming consequentially on the precipitated cementite plates [8]. However little evidence has been provided to support the assertion that this structure is bainitic, and the mechanism of transformation is not well understood [9]. Columnar bainite is another structure associated with hypereutectoid compositions. The morphology is of a nonlamellar arrangement of cementite and ferrite in the shape of "an irregular and slightly elongated colony", however the mechanism of formation is reconstructive [13]. It has been asserted that to call these latter two structures "bainite" is a misnomer due to their different mechanisms of transformation [9, 13, 14] although according to the generalised microstructural definition [15, 16], the description is accurate .

In order to avoid confusion, it is helpful to identify some of the agreed-upon, and notable, features of the bainite transformation, for which any theory must provide an explanation:

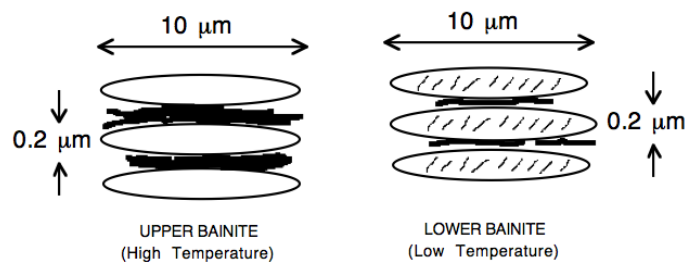1. **Upper and lower bainite**

Figure 1: The microstructural features of upper and lower bainite (from Bhadeshia). The dimensions are approximate and dependent upon factors such as transformation temperature and composition.

Bainite manifests in two distinctly different forms: upper bainite and lower bainite [17]. Upper bainite exhibits a characteristic lath shape, comprised of ferrite subunits of matching crystallographic orientation arranged in units called 'sheaves'. The subunits themselves are separated by carbide precipitates,

and can be of either plate or lath morphology.

The subunits in lower bainite tend to be coarser than those in upper bainite, but the two morphologies are similar as far as microstructure and crystallography are concerned. However, in lower bainite, the individual ferrite subunits also contain a fine distribution of carbide particles in addition to the inter-platelet carbides.

Figure 1 illustrates the essential differences between the two microstructures, and micrographs of upper and lower bainite subunits are shown in Figure 2. Upper bainite forms at higher temperatures (550-400°C) than lower bainite (400-250°C) in the same steel. The transition is also determined to an extent by the carbon content of the steel [12]. Mixtures of upper and lower bainite may be obtained by isothermal transformation.

2. **The bainite start temperature**

It can be demonstrated for many steels that there is a temperature B_S above which no bainite will form [19]. In some steels this corresponds to the bay in the TTT diagram between the overlapping curves of pearlite and bainite [20]. This temperature is well below that at which pro-eutectoid ferrite formation becomes thermodynamically possible.

3. **The incomplete-reaction phenomenon**

As the transformation temperature is reduced below B_S, the fraction of austenite that transforms to bainite is progressively increased [21]. However, during isothermal transformation, a limit is reached beyond which austenite will no longer transform to bainite, despite a significant quantity remaining untransformed. The reaction is said to be 'incomplete' since it is halted before the austenite achieves the equilibrium composition. The extent of the incomplete transformation in a given steel is composition-dependent: higher carbon contents will reduce the degree of transformation at a given temperature [22], although the phenomenon is difficult to detect in plain carbon steels.

(a)   (b)
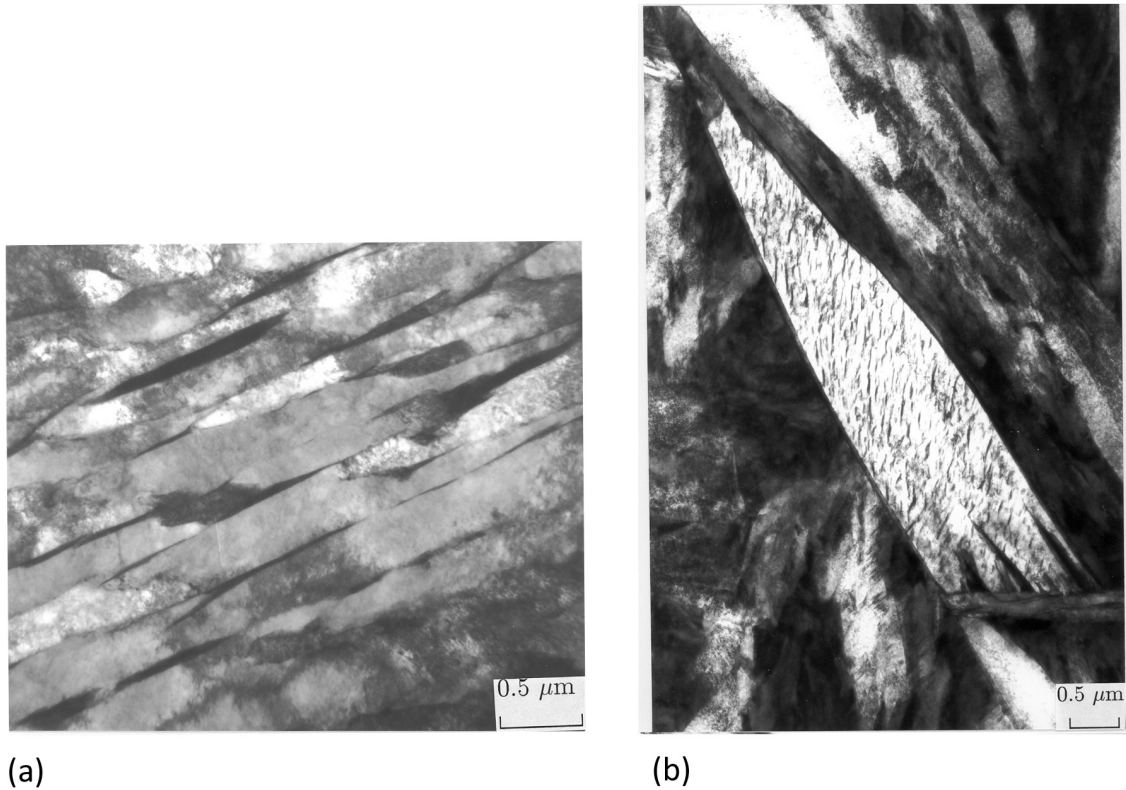
Figure 2: Transmission electron micrographs of (a) upper bainite subunits in a 0.095C-1.63Si-1.99Mn-1.97Cr steel and (b) lower bainite subunits in a 0.46C-2.10Si-2.15Mn steel. Image (b) shows carbide precipitation within the subunits themselves. From Chang and Bhadeshia [18].

2   The Origin of the Two Theories

The nature of the bainite transformation has been a subject of controversy ever since the bainitic microstructure was identified by Davenport and Bain in 1930 [15]. Figure 3 is a reproduction of the 'dark-etched, acicular microstructure' they observed. It was suggested that such a phase transformation "would occur just a little in advance of the carbide precipitation", via a process akin to that of the martensite transformation. The theory of a displacive mechanism of bainite formation had been proposed in 1926 by Hultgren [23] to explain observations of what he described as "needles of troostite" (but which was characteristic of a bainitic microstructure, troostite being the name then given to all fine mixtures of ferrite and cementite). First referred to as 'martensite-troostite' in the 1930 paper due to morphological similarities to martensite (see Figure 1.1 in [9]), bainite has maintained an association with the martensitic microstructure. Some have
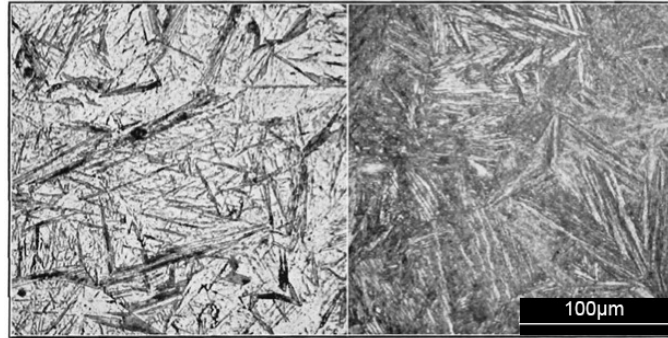
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Figure 3: The original micrographs of 'martensite-troostite' taken from the work of Davenport and Bain [15]

suggested that this initial case of mistaken identity influenced early theories of bainite formation [24, 25]. It is certainly true that some subsequent work expressed as a fact the assumption that bainite forms with a supersaturation of carbon [26, 27, 28]. One early example is the mechanism described by Vilella [29] as the rapid growth of flat plates of 'quasi-martensite' — supersaturated ferrite — which subsequently reject the excess carbon into the surrounding austenite at a rate dependent on the transformation temperature. This entire process was thought to last only a few millionths of a second. Vilella's work built upon the ideas of Davenport and Bain to form the beginnings of a diffusionless, displacive theory of transformation.

Robertson also made a direct observation of the bainite microstructure prior to the 1930 paper, but failed to identify it as a new structure [16]. At the time, interest was focused on 'intermediate microstructures'. Named martensite, troostite and sorbite, these microstructures were thought to form sequentially as transitional stages of the austenite-pearlite transformation. Robertson's detailed study of the relationship between these microstructures and cooling rate provided him with several micrographs of dark-etched acicular structures that he struggled to identify. He compared the bainite to pearlite, suggesting that the "complete change in the crystallography of the structures" was due to pearlite being nucleated by carbide, and bainite being nucleated by ferrite. He remained convinced that the growth of the Widmanstätten-like structures was limited by carbon diffusion. Much work to follow agreed with this hypothesis and many felt that a diffusion-controlled transformation was the correct explanation [17, 31, 32, 24].

The classification of bainite into two forms — upper and lower bainite — provided an opportunity for a

theory incorporating two different mechanisms of transformation. Indeed, it was suggested that upper bainite formed via a diffusion-controlled process, while lower bainite was formed via lattice shearing [17]. Similar theories would be put forward for many years to come, and will be discussed later.

3 A Thermo-Kinetic Explanation

Hultgren approached the problem of a displacive vs. a reconstructive mechanism by considering the shape of TTT-diagrams of various steels. The presence of two distinct C-curves suggested that two different transformation mechanisms were at work [31]. In the cases of alloy steels there was a clear break in the zero-line, which was interpreted as evidence of a change in transformation mechanism, although Hultgren did not believe the bainitic mechanism was diffusionless. However, his measurement of the alloy content of pearlitic cementite indicated that it had a higher alloy content than bainitic cementite (in the same steel), which shared the composition of the austenite. This is consistent with a diffusionless mechanism of transformation and led Hultgren to theorise that substitutional alloying elements do not participate in the bainite reaction.

One year earlier, in 1946, Zener had undertaken an analysis of the decomposition of austenite in which he assumed a diffusionless mechanism of bainite formation [28]. He arranged various alloying elements in order of their effectiveness in retarding the bainite transformation, and noted that this order was identical for both bainitic and martensitic transformations, implying that the two were "closely related". He saw that certain alloying elements were more effective at retarding the pearlite transformation than the bainite and martensite transformations. The ability to do this seemed to correlate to the carbide-forming tendency of these elements. Indeed, it was well-known that in high alloy steels the bainite reaction remained rapid even when the pearlite transformation was very slow [33].

This built upon work done by Davenport to elucidate the effect of alloying elements upon isothermal transformation curves [34]. He too had documented the severity of the retardation to be linked to carbide-forming tendency, although he also wrote that "in many instances these curves [are] so individual that it is very difficult indeed to summarize the trends except in a quite general way." Chromium, molybdenum and vanadium were strongest at limiting predominantly the pearlite transformation, while combinations of these and other

elements were found to have more complex effects. Cobalt, meanwhile, had the opposite effect: it accelerated the decomposition of austenite.

Zener's conclusion was that the alloying elements concentrated at nucleation sites, producing alloy carbides during pearlite formation. The subsequent segregation of the substitutional alloying elements slowed the transformation. However the effect of these elements on bainite and martensite was not believed to be related to nucleation, but rather to the free energy available for the transformation. The elements would affect the free energy of the system during pearlitic transformation as well, of course, but the dominant effect here was due to segregation. At the lower temperatures of bainite and martensite transformation, substitutional solutes are kinetically immobile, and so they cannot segregate to form alloy carbides. Their dominant effect was to alter the driving force for the phase transformations. Later, experimental work by Hultgren [31] and Murakami and Imai [35], as well as others, would support this theory.

Zener used the idea of free energy to explain the growth of bainite, by quantifying a T_0 temperature — the temperature at which austenite and ferrite of the same composition have the same free energy. Zener expressed the change in free energy of the system as a sum of three factors:

$$\Delta G = -\Delta G_{Fe^{\alpha\gamma}} + C\Delta G_{C^{\gamma\alpha}} - CT\Delta S_{C^{\gamma\alpha}} \qquad (1)$$

where
$-\Delta G_{Fe^{\alpha\gamma}}$ = the change in free energy of one mole of pure iron in the austenite phase compared to the ferrite phase
$C\Delta G_{C^{\gamma\alpha}}$ = the change in free energy of of one mole of carbon in the ferrite phase compared to the austenite phase (similar expressions may be included for other alloying elements, if present)
$CT\Delta S_{C^{\gamma\alpha}}$ = the excess of entropy of one mole of carbon when dissolved in austenite (this factor is negligible if the transformation proceeds quickly compared with the rate of carbon diffusion).

By setting ΔG equal to zero, it is possible to solve equation 1 for the austenitic carbon concentration in terms of the critical temperature. It is this line, plotted on an equilibrium phase diagram, that became known as the T_0 line. If one considers a steel of a given carbon content, the T_0 line represents a maximum

possible temperature for the bainite transformation: a B_S temperature. Similarly, for a fixed transformation temperature, the T_0 line limits the degree of transformation.

The limiting influence of the T_0 temperature on the bainite transformation was an important idea that had also been explored by Wever and Lange [36]. A consideration of the free energy of the system and of the equilibrium phase diagram serves to illustrate the key features of the theory (Figures 4 and 5).
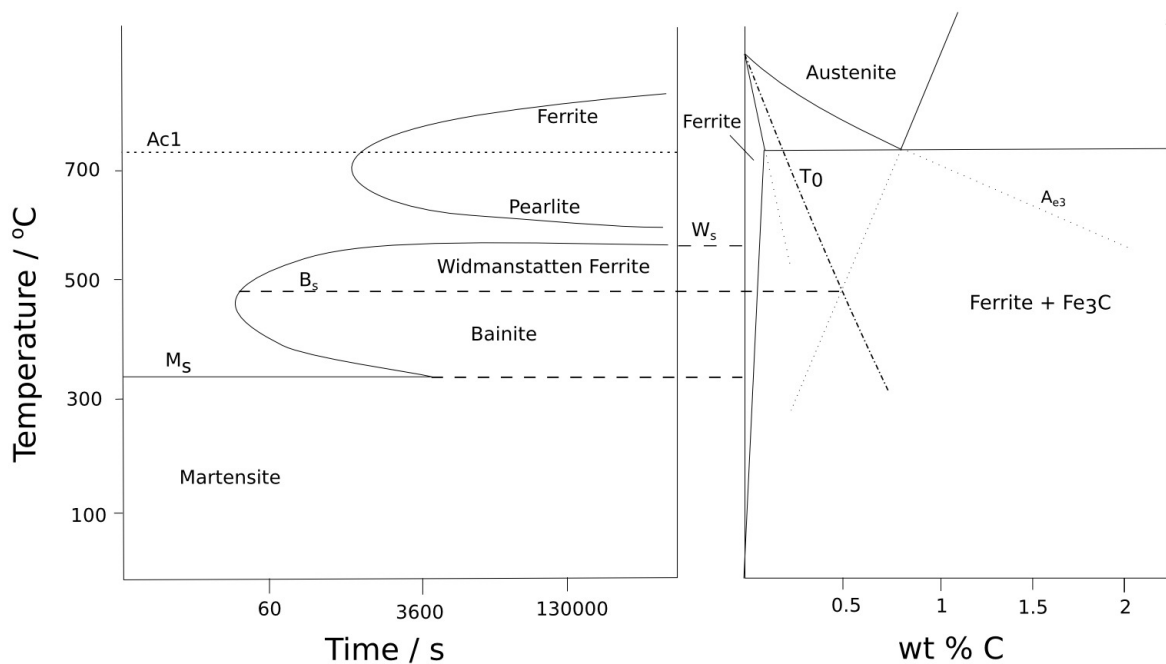

Figure 4: A sketch showing how the T_0 line determines the bainite start temperature, and how this is related to the phase diagram and corresponding TTT diagram.

During isothermal transformation, a subunit of bainite — supersaturated with carbon — grows from austenite. The excess carbon is subsequently rejected into the surrounding austenite, increasing its carbon content (assuming that carbides are not formed by precipitation). The next subunit of bainite must then nucleate and grow from carbon-enriched austenite, for which there is a slightly lower driving force. From Figure 5, it can be seen that, as the carbon content of the austenite continues to increase, the free energy available for transformation to bainitic ferrite will fall until it reaches zero at the T_0 line, and no more austenite will transform. It was suggested that this was responsible for the incomplete transformation phenomenon. In the
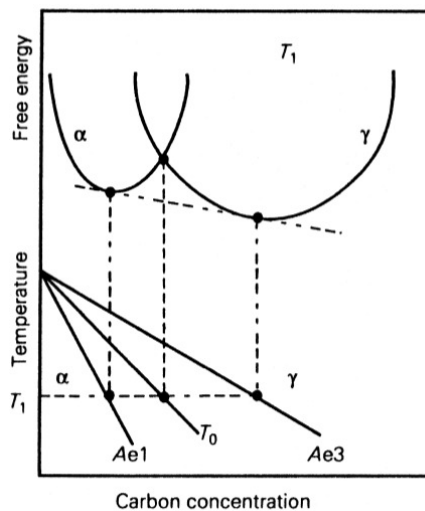
Figure 5: Illustration of the T_0 line on an Fe-C phase diagram, from Bhadeshia [9]

case of carbide precipitation, carbide film formation around the bainite subunits was thought to prematurely halt the transformation. That this occurs before the austenite reaches an equilibrium composition marked by the Ae_3 line is indicative of a diffusionless, displacive transformation.

Experimental results using 3% chromium steels agreed with the predictions of this theory [28] and were consistent with Davenport's observations. Zener was able to account for the anomalous behaviour of cobalt by noting that the quantity $\Delta G_{Co^{\gamma\alpha}}$ would be negative, rather than positive as it was for most alloying elements. The addition of cobalt would therefore increase the driving force for austenite decomposition.

As a result of his work, Zener claimed that a diffusionless mechanism of bainite formation could explain the incomplete transformation phenomenon, the B_S temperature, the variation in microstructure between upper and lower bainite and the effects of alloying elements. However, several researchers disagreed with the implication that the controversy had been settled. Troiano claimed that the bainite reaction was "time dependent and in this respect completely dissimilar to the martensite reaction" (although since martensite formation is a first order transformation it is also time dependent) [37]. Meanwhile, Klier insisted that the assumption of a diffusionless mechanism was due to a misunderstanding of the data presented in 1944 [21], instead claiming "incontrovertible evidence that a fluctuation of carbon concentration precedes the forma-

tion of bainite". His theory stated that these fluctuations would produce regions of low- and high-carbon austenite, so that austenite enrichment took place prior to the bainite reaction, via diffusion.

3.1 Comparisons with Martensite and Pearlite

As discussed in Section 2, the bainite microstructure was confused with martensite at the time of its discovery. When faced with a new decomposition product, it is understandable that the first step is to attempt to link it and place it relative to known morphologies. This was an approach taken by both schools of thought, with diffusive theories attempting to link bainite and pearlite together.

Interestingly, Zener also undertook a free energy analysis of the martensite transformation in his 1946 work, deriving an expression similar to equation 1:

$$\Delta G = \Delta G_{Fe^{\alpha\gamma}} + C\Delta G_{C^{\gamma\alpha}} + \Delta U \tag{2}$$

Here, in the case of rapid transformation, the entropy term is neglected and replaced with ΔU, representing the strain energy of the transformation. Once again, the ΔG term can be set to zero and thenceforth it is possible to relate a given carbon content to a critical temperature: the M_S temperature.

However, Zener stopped short of assuming that bainite was also formed via a shear transormation, like martensite. He chose to distinguish the martensite and bainite phases by the residual strains and stresses associated with the former, since he believed that bainite formation was not accompanied by strain [38]. According to him, it was only the alloying elements that did not diffuse during the bainite transformation. The process still required "the transfer of iron atoms from equilibrium positions on the austenite side of an interface to new equilibrium positions on the bainite side of the interface", but Zener was vague as to how this occurred. In some ways, Klier and Lyman took an opposite view to that of Zener. Although they proposed that carbon diffusion produced inhomogeneities in the austenite composition, they believed that the low-carbon regions would transform to supersaturated ferrite via a martensitic shear mechanism [21].

Hultgren, meanwhile, considered analogies with both martensite and pearlite. His work led him to de-

velop separate hypotheses for bainite formation in alloy and plain carbon steels [31].

In an alloy steel (as in all steels), martensite is formed without diffusion and inherits its composition from the austenite. Hultgren postulated a form of BCC iron that, at intermediate temperatures (i.e. those at which bainite formed), would inherit the *substitutional* alloy content from the austenite, while the carbon was still free to diffuse at a reasonable rate [31]. He named this metastable state 'paraequilibrium' and the ferrite 'paraferrite'. The growth of paraferrite would eventually be accompanied by the formation of 'paracementite' (also inheriting its composition from the parent austenite). He compared this to pearlite, formed in alloy steels via diffusion of all elements — a state he named 'orthoequilibrium'. Both morphologies, he suggested, underwent diffusion-controlled growth, becoming finer at lower transformation temperatures.

Hultgren extended his theory to the case of very low or zero carbon content alloys, in which martensite and paraferrite would be the same thing [31]. Troiano pointed out that this seemed unlikely since paraequilibrium transformation appeared to exclude the possibility of homogeneous shear that was characteristic of martensite [39]. Transformation curves as determined by Lyman and Troiano for 3% chromium steels seemed "to offer no chance of [the bainite and martensite curves] extrapolating to the same temperature at zero carbon content" [39, 22].

Where plain carbon steels were concerned, Hultgren took note of the theories of Robertson [16] and Mehl, which were based upon orientation observations of pearlitic and bainitic ferrite. Hultgren classified pro-pearlitic ferrite, bainitic ferrite and martensite as sharing a single orientation of ferrite relative to the austenite. He named this the primary orientation, to distinguish it from the orientation of pearlitic ferrite (which he called the secondary orientation) [40]. He also distinguished the orientations of pearlitic cementite and bainitic cementite with similar terms. Pearlitic cementite was of a primary orientation while bainitic cementite was of a secondary orientation [41].

Pearlite formation would begin with cementite nucleation and growth, followed eventually by the nucleation and growth of an adjoining ferrite particle. The presence of pearlitic cementite would encourage the ferrite to grow in its less-preferred (secondary) orientation. In contrast, bainite would nucleate with a particle of ferrite in the primary orientation, which would result in cementite precipitating and growing in its secondary

orientation. This theory implied that bainite was an 'inverse' sort of pearlite. The different transformation temperatures of pearlite and bainite were thought to affect the relative power of ferrite and cementite to influence the other's orientation. The possibility that this process could also occur in alloy steels was not ruled out. Some criticism of his ideas came from Dubé and Alexander [42] who believed that the 'orientation power' of ferrite and cementite should be independent of transition temperature.

4 Growth Rate and Surface Relief

Ko and Cottrell, in their 1952 work, approached the problem from a different angle, using hot stage microscopy to observe the growth of bainite in a range of alloy steels [43]. They found that the growth rate was slow compared with that of some martensitic transformations, and observed that bainite formation was a continuous, rather than an incremental, process. This indicated a diffusion-driven transformation. However, in the same study, they recorded a surface relief similar to that of martensite, and found that bainite plates did not cross austenite grain or twin boundaries. Both of these factors pointed towards a displacive transformation. Furthermore, the surface relief was indicative of strain, demonstrating Zener's earlier assumption to be incorrect.

In order to circumvent these contradictory observations, they proposed a new type of transformation to describe both bainite and martensite transformations. Named 'coherent transformation', it allowed for shear transformations subject to the kinetic limitations of carbon diffusion into the parent austenite. They suggested that at temperatures below B_S, there exists a driving force for decomposition of austenite into supersaturated ferrite, in terms of the free energy change of the system. However, additional driving force is needed to accommodate the increase in volumetric and shear strain energies incurred during martensite formation: this is therefore only possible at large undercoolings (i.e. below M_S). At intermediate temperatures, this strain energy could be reduced by lowering the carbon content of the supersaturated ferrite (either by carbide precipitation or diffusion), altering the energy balance and favouring transformation to an alternative product: bainite.

This placed bainite on a continuum with martensite, and also neatly explained the existence of upper and lower bainite (in upper bainite, carbon is removed predominantly by diffusion; in lower bainite, by precipita-

tion). The presence of carbide-forming alloying elements was thought to 'anchor' clusters of carbon atoms, reducing their mobility and thus slowing the growth of bainite. Within this framework, the distinction between bainite and martensite moved from being based upon strain to being based upon the presence or absence of carbon diffusion.

Ko and Cottrell's growth rate measurements were later confirmed by other publications [44, 45] and seemed to point conclusively towards a diffusion-controlled transformation. Zener's equation governing diffusion-controlled edgewise growth of a plate was modified by Hillert, who applied it to Widmanstätten ferrite and bainite [8]. After some further refinements [24, 46, 47] and comparison with experimental data [48, 49] it seemed that the measured growth rates were slightly lower than those predicted by carbon diffusion, allowing ferrite of both types to grow at a rate low enough to avoid supersaturation of carbon.

Meanwhile, those supporting the diffusionless paradigm concentrated on the surface relief evidence. Confusingly, further studies revealed that Widmanstätten ferrite (thought to form via diffusion) also produced a surface relief [50]. Many attempts were made to reconcile or explain away the conflicting results.

In particular, Oblak and Hehemann, in 1967, examined the structures of Widmanstätten ferrite and bainite more closely [51]. Their electron micrographs revealed that Widmanstätten ferrite formed as single crystals, while upper bainite plates consisted of much smaller subunits. They concluded that there was no evidence that Widmanstätten ferrite and bainite formed via the same mechanism. This meant that the presence of a surface relief could not be used as evidence of a diffusionless mechanism. Although this seemed to deal a blow to the diffusionless theory, the authors proposed a mechanism of bainite formation whereby the individual subunits grew rapidly via a diffusionless, displacive transformation. The growth rate of bainite was limited not by diffusion, as had been believed, but by the rate of nucleation of these subunits. The shape and size of the subunits was restricted by the displacement strain accumulated during growth. In this way, a plate-like sheaf of bainite could be "formed by the sympathetic nucleation of successive subunits" (Figure 6).
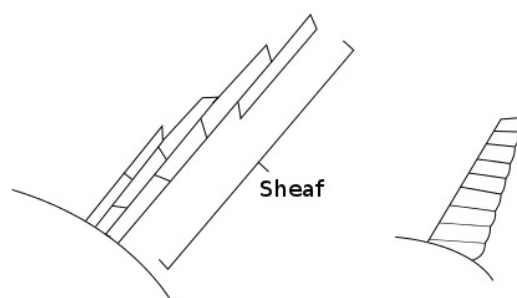
Figure 6: Sketches of two possible structures formed by the repeated nucleation and growth of subunits as postulated by Oblak and Hehemann [51].

5 A Crystallographic Approach

The discovery of uniformly-distributed ϵ-carbides [51, 52, 53] (which had never been observed to precipitate from austenite) in lower bainite was consistent with the belief that bainitic ferrite forms in a supersaturated state. Using dilatometric techniques, Deliry [53] measured the amount of ϵ-carbide in lower bainite and found it equivalent to the total carbon content of the steel. These observations indicated that a displacive mechanism was at work, although they did not exclude the possibility that the shear mechanism was diffusion-controlled.

The method of carbide formation in upper bainite was less clear. The presence of a large quantity of carbon-enriched austenite suggested a diffusional mechanism [51], but crystallographic evidence [54, 55] seemed to point towards carbide precipitation from carbon-enriched austenite following a displacive, diffusionless transformation. Whether this precipitation takes place during or after the bainite transformation, however, was a puzzle that was to remain unsolved.

The general understanding followed Christian [56], who accepted that lower bainite formed from ferrite supersaturated with carbon but upper bainite did not. It was therefore suggested that "the crystallography of upper bainite should match that of low-carbon martensite while that of lower bainite should match the crystallography of martensite (in the same alloy)".

Following from Ko and Cottrell's surface relief observations, further work had characterised the bainite

shape change as approximately an invariant-plane strain (Figure 7), similar to that associated with martensitic transformation [57]. Furthermore, evidence showed that the austenite and ferrite were related by a Kurdjumov-Sachs relationship in both bainite and martensite [55, 58]. This led Srinivasan and Wayman, in 1968, to undertake a phenomenological analysis of the lower bainite transformation [59].
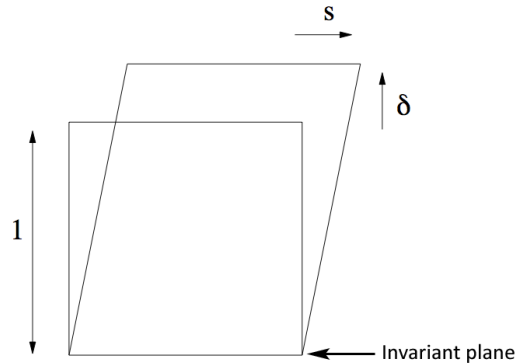

Figure 7: Schematic of an invariant-plane strain. The invariant plane is the habit plane and the displacement consists of a tensile component (δ) and a shear component (s), producing a homogeneous distortion. In the case of martensitic transformation, the IPS results from a combination of the Bain strain [60] and a lattice invariant shear deformation such as slip or twinning.

Alongside this, they carried out TEM and X-ray work, hoping to measure crystallographic parameters (habit plane and specific variant of the austenite-ferrite orientation relationship) for comparison with their theoretical work [61, 59]. They found that, while martensite often exhibited internal twinning, there was no evidence that it occurred during the bainite transformation. The orientation relationship of the carbides in bainite pointed towards the presence of slip planes predicted by the theory to be operative during formation, which supported the conclusion that bainite formed via shear and stepwise growth. Moreover, the discovery that bainite forms as platelets in three dimensions bolstered the case for a displacive transformation, since one would expect a parallel arrangement of plates from a diffusive process. Overall, their practical and theoretical work agreed well, and seemed to indicate a shear transformation mechanism for lower bainite.

These results were questioned by Kinsman and Aaronson (in a debate with Hehemann) [2], who argued that the agreement between observed crystallography and phenomenological theory was only possible by assuming a contraction of the ferrite lattice during transformation — something they did not accept was

correct. Srinivasan and Wayman, along with Edwards and Kennon [62] found no similarity between the orientation relationships and habit planes of lower bainite and martensite. Kinsman and Aaronson therefore concluded that "neither upper nor lower bainite forms by a martensitic mechanism". Instead, they promoted a growth mechanism involving the propagation of ledges controlled by a diffusive process [63]. The principle was validated by the work of Laird and Aaronson on aluminium alloys [64, 65], so it became a question of whether it was also applicable in ferrous alloys.

Nemoto's 1974 work [66] confirmed the results of Kinsman and Aaronson, who had used thermionic emission microscopy to show that bainite growth was continuous and did not occur in steps [2]. However, his results also revealed the formation of dislocations in and around the bainite, characteristic of a plastic relaxation accompanying a displacive shape change. Hehemann, meanwhile, argued that the lack of twinning in bainite was responsible for the variation in habit plane, and did not rule out a displacive mechanism [2]. Although the data was specific to lower bainite, Hehemann believed the conclusions could be applied to upper bainite also. Referring back to Ko and Cottrell [43], he insisted that "the question of the continuity of the growth process is independent of the growth mechanism": slow continuous growth rates could equally support a shear mechanism controlled by carbon diffusion.

Although bainite was often compared with martensite, the similarities between bainitic ferrite and Widmanstätten ferrite were also especially strong, leading some to argue that there should not be a distinction between the two [43, 25]. Others attempted to demonstrate how the two phases could achieve such a similar appearance via different transformation mechanisms [67, 68, 69, 70, 71].

There was much evidence to suggest that the surface relief of Widmanstätten ferrite corresponds to an invariant-plane strain with a large shear component [67]. Questions arose as to whether a ledge mechanism as proposed by Aaronson could produce such surface relief [67]. Instead it was found that the observed surface relief was in good agreement with the predictions of the Bowles-Mackenzie crystallographic theory [57], suggesting that Widmanstätten ferrite grew with a displacive mechanism. It certainly seemed that the presence of an invariant-plane strain was at odds with a diffusional or massive transformation [72, 73]. However, Aaronson *et al.* demonstrated that it was thermodynamically impossible for Widmanstätten ferrite to form via a shear mechanism [68]. McDougall disagreed with this analysis, pointing out a flaw in their

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assumption that the ferrite would be elastically accommodated [69]. He asserted that plastic relaxation would relieve the elastic strain energy under transformation conditions, thus overcoming the thermodynamic barrier.

In 1980, Bhadeshia interpreted the Widmanstätten crystallography as indicative of back-to-back displacive growth of mutually accommodating ferrite plates [70]. He went on to develop a kinetic theory of nucleation and growth, whereby both Widmanstätten ferrite and bainitic ferrite underwent carbon partitioning at nucleation, but only bainitic ferrite grew without diffusion, instead rejecting carbon into the austenite after the transformation was complete [71]. This implied that, at nucleation, the two forms were identical, and the formation of bainite was dependent upon the availability of a sufficient driving force to sustain supersaturation during growth. Although the bainitic ferrite would appear virtually identical to Widmanstätten ferrite, the stored energy of bainite was expected to be significantly higher. The equilibrium carbon content of the bainite nucleus, in contrast to the supersaturated martensite nucleus, was thought to explain the differences in crystallography between those two microstructures.

6   A Mechanism-Based Theory for Bainite Nucleation and Growth

The crystallographic incongruities having been tackled, the problem returned to one of carbon diffusion. Bhadeshia and Edmonds argued strongly for the diffusionless case [74, 75]. Their electron micrographs of a silicon steel revealed lenticular subunits separated by retained austenite of the same crystallographic orientation. The observation of subunit growth even when carbide formation was suppressed implied that the subunits could not be compared with ledges, since they were individually isolated by carbon-enriched austenite films. The addition of silicon was an important step, since it allowed the study of the austenite-ferrite transformation without the interference of carbide precipitation.

The size of each subunit was limited by a frictional stress associated with the plastic accommodation of the shape deformation, such that constant nucleation of new subunits was required to propagate a sheaf [74]. This growth occurred via sympathetic nucleation at the tips of fully formed subunits. It was shown that this was energetically more favourable than nucleation adjacent to the subunits; by nucleating at the tips, the new subunits could avoid the carbon-enriched regions formed by diffusion from complete subunits [75]. The total volume fraction of bainite formed was limited by the T_0' line.

The T_0' line is a modification of the T_0 line that includes the strain energy of the bainite transformation. It was first proposed by Le Houillier *et al.* [76] and represents the point at which the free energies of austenite and ferrite of the same composition are equal, once this strain energy has been incorporated into the calculation. The value of the strain energy was calculated to be 400 J mol^{-1} [71]. The difference between T_0 and T_0' was considered to be negligible by some [77], and some subsequent research continued to refer to T_0, neglecting strain energy. This approach would later be criticsed by Hillert, whose own calculations pointed to a significant difference between T_0 and T_0' [78].

Although the work of Bhadeshia and Edmonds did not account for carbide precipitation, it was emphasised that it was a process in direct competition with carbon rejection into residual austenite. If this were the case, it would explain why the incomplete transformation phenomenon was difficult to detect in plain carbon steels, where precipitation processes dominate. In alloy steels, the suppression of cementite, and kinetic barriers to the formation of alloy carbides (even those thermodynamically more stable than cementite, e.g. $Cr_{23}C_6$) minimise the presence of precipitation, so incomplete transformation is readily observed.

This and other work [79] was consolidated into a mechanism-based theory for the bainite reaction [80]. It was able to reproduce the effects of various alloying elements (Ni, Si, Mn, Cr) on the shape of TTT curves and transformation kinetics. However the authors themselves noted that the predictive ability of their theory was somewhat limited by an inability to account for "secondary effects" of these elements. Nevertheless, it was a good starting point and would continue to be improved over the following years [81, 82, 83, 84, 85].

7 Experimentally-based Criticisms

Since the 1950s, there had accumulated a great deal of experimental evidence showing 'solute-induced diffusional drag on grain boundary motion' ('solute drag') [86, 87, 88, 89, 90]. The original work of Lücke and Detert [91] had postulated that grain boundaries represented low energy regions for impurity atoms. These atoms would therefore segregate and diffuse in the boundary, exerting a dragging force on the grain boundary as it continued to grow. However despite much development of the accompanying quantitative theory it still could not be generalised to any interphase interface [92]. Some variations of this theory required segregation

of alloying elements to the transformation interface. This idea was used to reconcile a diffusional transformation with observed incongruities in the kinetic measurements of the bainite transformation, for example: the incomplete transformation phenomenon [1, 2, 93].

The solute-drag concept was not the only diffusion-controlled model that had been applied to the bainite transformation. The local equilibrium model [94] assumed a constant partial molar free energy among elements across the austenite-ferrite interface. This requires both the alloy and carbon atoms to partition during transformation. In the case of highly-supersaturated phases, the local equilibrium model also demands a narrow concentration spike for alloy elements in the interfacial austenite, in order that the alloy concentration at the interface match the equilibrium value [32].

Paraequilibrium transformation, in contrast, requires only partial supersaturation and no redistribution of substitutional alloying elements across the transformation interface (as first suggested by Hultgren [31]). Carbon partitions during transformation to maintain a constant partial molar free energy across the interface, while the X atoms, with a much lower diffusivity than carbon, do not. In the case of ferrite, the model implies that growth is controlled by carbon diffusing across the interface, in accordance with equilibrium conditions, whereas the atomic X:Fe ratio is constant across the interface and remains so for the duration of the transformation.

These theories were reviewed carefully by Bhadeshia and Waugh [79, 95], who used atom-probe imaging to examine the distribution of various elements across a bainitic ferrite-austenite interface. They found no evidence of a compositional spike of alloy elements, neither did they detect (substitutional) solute segregation, in direct contradiction to the theories of local equilibrium and solute drag. On the contrary, it has been demonstrated that there is no difference between the substitutional alloy element content of bainite and that of the parent austenite [96, 97, 98].

They also undertook a thermodynamic analysis of the incomplete transformation phenomenon, assuming a paraequilibrium mechanism. The calculated levels of carbon supersaturation in the ferrite during growth were too high to be physically feasible, indicating that the paraequilbrium hypothesis may also be invalid [79].

Most exciting, however, was the use of hot-stage microscopy to observe the growth of individual subunits of bainite [95]. The measured growth rate under these conditions at 380°C was 75 μm s^{-1} — about three times faster than the maximum growth rate allowed by diffusion, as calculated using Trivedi's theory [47, 99]. This seemed to put paid to the idea that the bainite transformation was diffusion-controlled, and provided direct evidence for Oblak and Hehemann's theory. However, the work has been criticised as being merely 'preliminary', with no subsequent follow-up or further work being published [25]. Many instead pointed to the larger body of work showing lower growth rates. Goodenow [45] had worked at a lower resolution than Bhadeshia, who had also made his measurements at higher temperatures (380°C) than Speich [44]. Speich attempted to model the growth rate for temperatures greater than 320°C, but Goodenow's work shows that the temperature dependence of growth rate may change at higher transformation temperatures. Later reviews expressed the view that many of these low growth rates may have been a result of measuring the growth of a sheaf of bainite, rather than of a subunit [100].

Hillert had carried out a similar analysis of the diffusionless theory in low-alloy steels. He created a model to demonstrate that there is negligible supersaturation of ferrite until the interface velocity reaches a certain critical point [24]. He argued that the growth rates required to initiate supersaturation are higher than those typically obtained at bainitic transformation temperatures, concluding that supersaturated growth cannot occur. Instead he demonstrated that the growth of both Widmanstätten ferrite and bainite can be accounted for by carbon diffusion, and that this is supported by evidence of no change in the edgewise growth rate between the two types of ferrite that could indicate a change in transformation mechanism. Hillert also suggested that, as bainite transforms at progressively lower temperatures in alloy steels, the interface might become more coherent. This would lower the diffusivity of the alloying elements such that it was possible for no 'compositional spike' to develop at the interface [101].

Hillert combined his diffusionless model with the work of Ohmori and Maki [102] and Steven and Haynes [103] on Fe-C alloys. He first validated the model using M_S data (Figure 8(a)): he took a value of 600 J mol^{-1} for the driving force [104] and assumed a diffusionless, adiabatic transformation, achieving quite good agreement with experimental M_S values taken from Ohmori and Maki. By comparing B_S data with the calculated T_0 line (Figure 8(b)), he showed that the B_S data bore no relation to the T_0 line. Although the data for B_S are not very extensive in this case, these results indicated that neither T_0 nor T_0' corresponds to B_S as the diffusionless theory predicted.
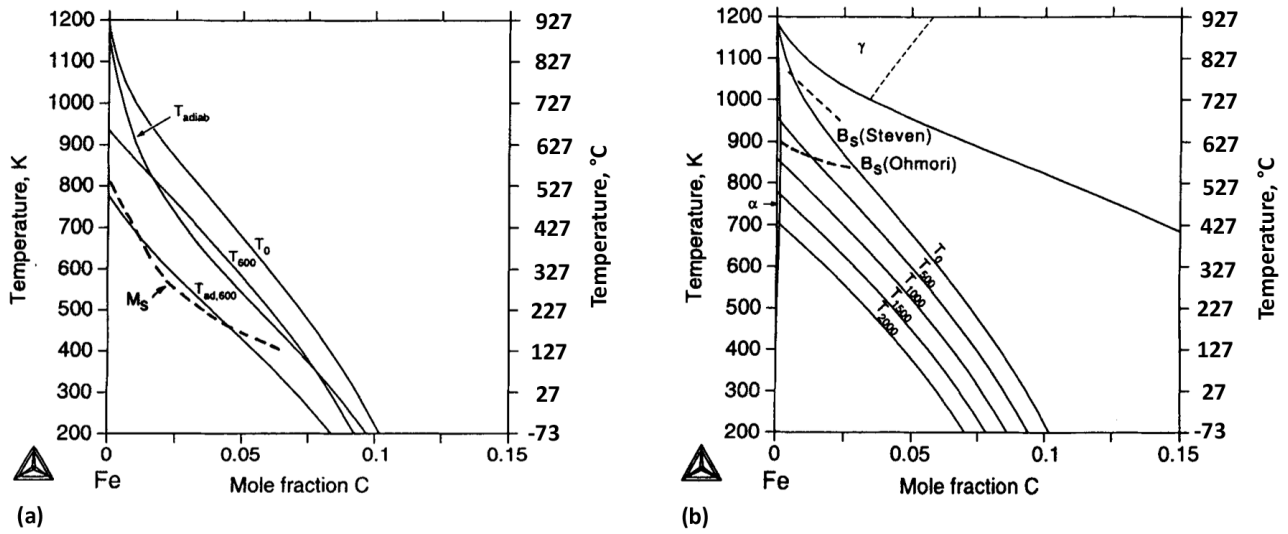
Figure 8: (a) Use of Hillert's model [101] to predict the M_S temperature (b) comparison of calculated T_0 curves and experimental B_S data. In each case lines have been drawn parallel to T_0 to account for various values of strain energy. T_0' as discussed by Bhadeshia corresponds approximately to the T_{500} line in (b).

However, a study of the transition of upper bainite to lower bainite in plain carbon steels of 0.2-1.8 wt%C [105] revealed a link between the microstructural transition temperature (MTT — the point where upper bainite is replaced by lower bainite) and T_0 (Figure 5 in reference [105]). The work revealed that the MTT line was shifted relative to the T_0 line; this difference was taken to represent the non-chemical free energy for displacive growth of lower bainite, although the authors do not go into detail.

Of further interest was the finding that, below 0.35 wt%C, no lower bainite formed at all. This was significant since it agreed with the predictions of models that balanced the decarburisation by diffusion of supersaturated ferrite against cementite precipitation kinetics [106]. Ferrite is assumed to grow in the supersaturated state, and the excess carbon is subsequently rejected into austenite. Upper bainite is expected to predominate at lower carbon contents, whereas at higher carbon contents, some carbon may also precipitate within the ferrite sheaves themselves, forming lower bainite.

Curiously, although the authors contended that "the bainitic transformation is essentially martensitic", Figure 5 in reference [105] clearly shows that upper bainite was observed to form above the T_0 curve: something

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precluded by the displacive theory. The lower bainite transformation, on the other hand, is restricted both by the T_0 curve and by a maximum temperature (350°C) at lower carbon contents (in agreement with the presumption that upper bainite will dominate at these compositions). However, in an earlier paper [107] the same hypereutectoid data is presented and indicates that no upper bainite was observed, which *is* in accordance with the displacive theory. It is likely that the authors have neglected to label the pearlite region in their later paper.

The authors also highlighted the morphological similarities between martensite and bainite and used morphological features to distinguish upper and lower bainite. Martensite morphology undergoes a composition-dependent change: from needle- or plate-like (high C%) to feather- or lath-like (lower C%). Oka and Okamoto accordingly classified their bainitic microstructures as either 'feathery' (upper bainite) or 'needle' (lower bainite). They noted that the constant MTT corresponded to the M_S at which the martensite also undergoes a morphological transition.

The predictions of the displacive model were consistent with the results of other experimental work. Srinivasan and Wayman [108] had found that upper bainite did not form at all in a Fe-7.9 Cr-1.1 C wt% alloy. Conversely, no lower bainite phase was found in high purity Fe-C alloys with a carbon concentration below 0.4 wt% [109]. The model also explained the occurrence of intragranularly nucleated upper bainite — but never lower bainite — in welds. The typically low carbon content of weld metals would be expected to favour the formation of upper bainite over lower bainite. This had been confirmed in 1989 when Sugden and Bhadeshia achieved intragranular lower bainite ('lower acicular ferrite') by deliberately increasing the carbon content of such alloys [110].

In 1990, the International Conference on the Bainite Transformation provided a platform for research on the incomplete reaction phenomenon. In a series of papers, several workers presented evidence disputing that the incomplete reaction phenomenon ("transformation stasis") was a general characteristic of all bainitic transformations [111, 112, 113]. They adapted the solute drag idea to explain why the bainite transformation apparently stopped in certain alloy steels — and did not seem to be inhibited at all in others. The solute-drag-like effect (SLDE) described how certain alloying elements (typically Mo, Mn, Cr) segregate to an austenite-ferrite interface and alter the carbon concentration gradient in austenite, thereby slowing the

rate of ferrite growth [111]. Of five alloying elements studied (Ni, Cu, Si, Mn, Mo), only steels containing Mn or Mo showed signs of incomplete reaction [112, 113]. Since only Mn and Mo are able to significantly lower the activity of carbon, Reynolds *et al.* [112] concluded that "incomplete transformation is a manifestation of the SDLE."

It may, however, be premature to infer that these observations are not in accordance with a displacive theory. In several of the experiments, carbide precipitation was not suppressed and secondary reaction products were present, which would affect the carbon concentration of the austenite and possibly prevent any incomplete reaction occurring. The authors chose to use a microstructural definition to identify bainite: "nonlamellar...ferrite" or " any nonlamellar eutectoid decomposition product", which does not provide for a distinction between bainite, Widmanstätten ferrite and proeutectoid ferrite.

The work by Reynolds *et al.* also served to highlight a strong similarity between the displacive and diffusional theories [112]. The authors suggest that bainitic ferrite consists of 'sheaves', which themselves grow via 'sympathetic nucleation' of smaller ferrite crystals: a process which seems similar, if not identical to, autocatalytic nucleation. In the diffusional case, the growth of these individual crystals is limited by the SDLE; in the displacive case, subunit growth is halted by plastic deformation in the adjoining austenite. Reynolds *et al* explain:

> "When carbide precipitation does not occur, the formation of ferrite is necessarily accompanied by carbon enrichment of the austenite adjacent to the ferrite crystals. The higher carbon concentration in this austenite lowers the driving force for sympathetic nucleation of ferrite, and transformation stasis results when sympathetic nucleation ceases [113]. Stasis ends when carbide precipitation restores ferrite growth by relieving the SDLE and by locally increasing the supersaturation for ferrite growth."

Another interesting piece of evidence in favour of the diffusional theory came from Spanos, who carried out extensive TEM work and examined that of others, concluding that the crystallographic evidence was inconsistent with the displacive model [114]. He observed that cementite in lower bainite (in a 0.6 C-4.02 Mn-2.02 Si alloy) showed good atomic matching with both the ferrite and the austenite phases, and this was supported by similar observations from other researchers [61, 115]. Following also the work of Shackleton

and Kelly [55], Spanos concluded that such a three-phase crystallographic correspondence was indicative that cementite precipitated from the austenite. However the conclusions reached in this work claimed that these observations could be explained "equally well" by a diffusive theory rather than flatly contradicting the displacive theory. Crystallographic matching between all three phases is not always present [75] and there are several variables in the work by Spanos whose effects are unknown.

The evidence presented in support of a diffusional theory was certainly compelling, but not conclusive — although the same could still be said of the displacive theory. By the mid-1990s, however, the displacive theory of the bainite transformation had become sufficiently developed to enable its implementation in the design of new steels [116, 117]. This by no means guaranteed that it was in fact correct, but certainly it proved its usefulness.

8   Surface Relief Revisited

In 1996, Swallow and Bhadeshia revisited the issue of surface relief [118]. Since Ko and Cottrell, many attempts had been made to quantify experimentally and theoretically the invariant-plane strain [61, 75, 119, 120]. It was not until 1982 that a value for the shear component of the strain was determined that agreed with the theory [121]. Swallow and Bhadeshia confirmed that this value was approximately equal to 0.26. The existence of such a large shear component pointed towards a deformation involving the co-ordinated movement of atoms, which required a coherent, glissile interface.

Atomic force measurements revealed plastic deformation in the austenite adjacent to the bainitic ferrite subunits (Figure 9). This does not usually occur in martensite, which tends to be accommodated elastically. The higher temperature of the bainite transformation lowers the yield strength of the austenite, producing plastic behaviour. This is a crucial point: the deformation of the austenite prematurely halts subunit growth before they impinge on an obstacle. As a result, a new subunit of bainite must nucleate to propagate the transformation further, forming the characteristic sheaf morphology.

A further piece of evidence in support of the displacive paradigm was presented in 1999. It was shown that heavy deformation of austenite retards its subsequent decomposition into bainite [122]. In a reconstruc-
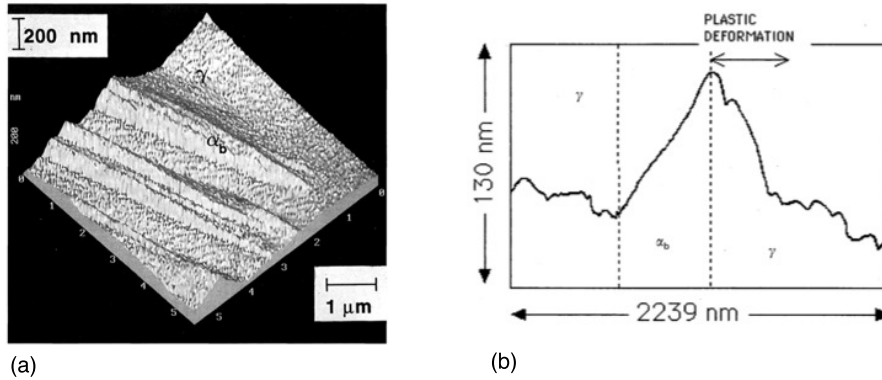
Figure 9: (a) Atomic force microscope image of several bainite subunits, showing plastic accommodation in the adjoining austenite (dark patches). (b) Atomic force microscope scan across a bainite subunit, showing similar plastic deformation. From Swallow and Bhadeshia [118].

tive process, such deformation always leads to an accelerated transformation. This is because the generated defects act as additional nucleation sites, providing extra driving force, and are then eliminated by the growth of the new phase. During a displacive transformation the defects are inherited by the new phase. it was found that, in the case of bainite, the transformation rate initially increases, but then falls. This was thought to be impossible for a reconstructive process [122], and provided a compelling argument in favour of a displacive transformation.

9   Support for a Diffusional Mechanism

Despite the evidence to the contrary, there was still much support for a diffusion-controlled bainitic transformation via a ledge mechanism [123, 124, 125, 126, 127]. The work of Nemoto [66] was held up in contradiction to the work of Bhadeshia and it was maintained that the majority of experimental work showed interface velocities corresponding to diffusion-control [123].

The STM and AFM observations of Fang [128], which revealed a 'tent-like' bainite surface relief on a sub-unit scale (Figure 10) — as opposed to that of the invariant-plane strain seen by Swallow and Bhadeshia — were taken as evidence of a diffusive, ledgewise process. Subunits of this type were expected to form via such

a mechanism, which had previously been shown to be favourable under certain conditions: higher carbon contents and lower transformation temperatures [129].
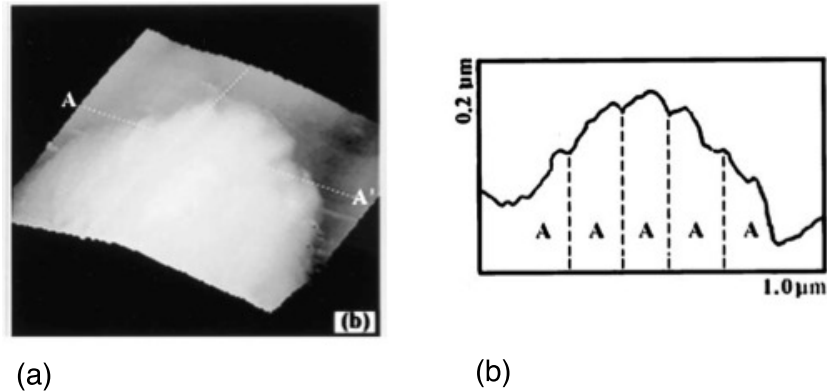

Figure 10: (a) Atomic force microscope image of a bainite subunit. (b) Atomic force microscope scan across the subunit AA', showing a tent-like surface relief. From Fang [128].

Hillert insisted that there was no clear experimental evidence of either the supersaturation of newly-formed bainitic ferrite or the high growth velocities characteristic of martensitic transformations [123]. He and others continued to favour an alternative framework, within which bainite and Widmanstätten ferrite comprised a continuous spectrum of acicular ferrite [8, 78], as evidenced by the continuous smooth gradation of growth rate and critical carbon content between the two forms [24]. Several workers proposed kinetic models based upon these ideas — among them Quidort and Bréchet [130]. It has been noted that the weakness of such models lies in the adoption of the solute-drag effect in order to explain certain aspects of the kinetics [100, 131, 132]. Mo segregation is also invoked, yet high-resolution analysis supports Bhadeshia's previous result that no segregation of alloying elements occurs at the transformation interface [97, 133]. While the work of Humphreys *et al.* seemed to contradict this, the transformations that they studied occur at temperatures at which substitutional solutes would be mobile, and the transformation product appears to be proeutectoid ferrite rather than bainite [134].

In 2004, Hillert *et al.* modelled the thermodynamics of diffusion-controlled growth of acicular ferrite [78]. They examined the Fe-C-Si system (2.01wt% Si used to eliminate carbides), extrapolating growth rate data to zero to plot the critical limit for acicular ferrite growth (Figure 11). Agreement with experimental results

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was good and the analysis was extended to examine the effects of other alloying elements: Mn, Cr, Mo and Ni. When compared with Bhadeshia's approach [75], based upon the T_0' curve (also in Figure 11), it seemed clear that the diffusional model gave better agreement with the experimental data. However the authors noted that Bhadeshia used a different thermodynamic database to calculate T_0' — one which gives different results compared with those presented by Hillert.
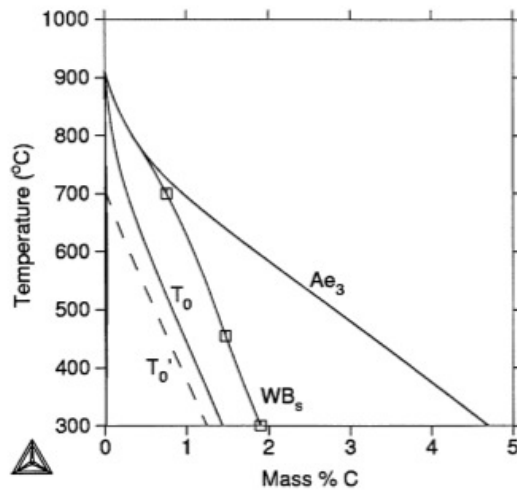

Figure 11: Predicted B_S according to Hillert [78]. Here it is designated WB_S as it represents the limit above which acicular ferrite cannot grow. This work considers bainite part of a continuous spectrum of acicular ferrite, along with Widmanstätten ferrite. The square symbols indicate experimental data and show bainite growth above the T_0 limit.

Hillert's method was able to predict the growth limits in Fe-C alloys as well as the effects of austenite-stabilising elements. The analysis indicated that the thermodynamic effects of these elements (Ni and Mn) "would be much weaker [than they observed experimentally] if ferrite is assumed to inherit the carbon content of the parent austenite". The limitations of the diffusional approach, meanwhile, lay in its inability to accurately predict the effects of Cr and Mo, once again relying on solute-drag to explain the discrepancies.

10   Validation of the Displacive Theory

The work and ideas behind the displacive mechanism were soon consolidated into a rigorous kinetic theory [85]. Classical nucleation theory was not adequate to describe the nucleation mechanisms involved in the bai-

nite transformation [71]. With refinement to allow for the distinction between grain-boundary nucleation and autocatalytic nucleation, the theory was "able to generate accurate predictions of isothermal and continuous cooling transformation curves" [85]. In addition, the displacive theory continued to be applied successfully to steel design [135, 136, 137].

With the availability of more sophisticated imaging and characterization techniques, evidence in support of the displacive mechanism increased markedly. X-ray analysis confirmed that the bainite transformation was limited by the T_0' curve: that the retained austenite was enriched in carbon to a degree predicted by the curve [9, 98, 138]. Atom maps verified that no segregation of substitutional solutes occurred during transformation in high-C high-Si alloys and, for the first time, revealed the presence of Cottrell atmospheres in bainitic ferrite [98]. This confirmed Bhadeshia's earlier prediction that Cottrell atmospheres at the transformation interfaces would hinder the bainite transformation [75], which explained the increased size of subunits at lower carbon contents.

It had been known for some time, as a result of X-ray analysis [137, 138, 139], atom probe analysis [79, 97, 133] and convergent beam electron diffraction analysis [140], that the carbon content of bainitic ferrite following transformation remained higher than predicted by paraequilibrium (i.e. allowing for only the carbon to partition after the transformation). This was accounted for by the trapping of large amounts of carbon at dislocations around the ferrite-austenite interface [98]. Cottrell atmospheres also provided a possible explanation as to why ϵ-carbide is not always detected as a precursor to cementite precipitation in lower bainite. The ϵ-carbide is thought to be the first stage in cementite precipitation sequence in lower bainite [141], but is sometimes missed out in the case of high-carbon, high-silicon steels (despite the fact that silicon is expected to favour the formation of ϵ-carbide) [74, 98]. Caballero was able to explain this phenomenon by demonstrating that the carbon is instead "tied up at the dislocations."

Synchrotron X-ray studies revealed the nonuniform stresses generated by the displacive transformation and were able to demonstrate unequivocally that "the austenite remains homogeneous prior to the bainite transformation, and that the reaction remains thermodynamically incomplete" [142]: that is, there is no carbon rejection into the austenite before transformation, and the reaction does not go to completion as expected from the phase diagram. The observed change in the austenite lattice parameter prior to transformation was

consistent with carbon partitioning between austenite and bainitic ferrite during nucleation, and provided strong evidence in support of ferrite supersaturation [142].

Borgenstam and Hillert continued to argue in favour of diffusion-controlled growth, choosing to pursue a metallographic argument [25]. They showed that the 'overlapping' of lower bainitic subunits observed by Oblak and Hehemann [51] is analogous to the way sub-colonies overlap in ledeburite. Because ledeburite forms gradually via carbon diffusion and ledge propagation, the inference was that bainite must undergo a similar transformation to achieve the 'overlapping' morphology.

The authors also pointed out that the lamellar appearance of ferrite and cementite in lower bainite subunits resembled pearlite, and was indicative of cooperative growth. They provided micrographs purporting to show carbide-free sections of ferrite inside a bainite plate, and claimed that these sections were the regions from which the rest of the structure had originally formed. Finally, they compared upper bainite to Widmanstätten ferrite and concluded, based on observations of surface relief and plate morphology, that bainitic ferrite and Widmanstätten ferrite are identical. Among the conclusions in this work, the authors stated that

> "it seems that one should now abandon the idea about bainitic ferrite being supersaturated when first formed."

However, soon afterwards, atom probe tomography revealed for the first time the supersaturation of and subsequent carbon rejection from bainitic ferrite in the earliest stages of transformation of a high carbon, high silicon nanocrystalline steel [143]. Later work confirmed these results and also provided additional evidence of plastic relaxation due to the shape change accompanying the bainite transformation [144].

10.1   The Design of New Bainitic Alloys

Part of the value of a theory of the bainite transformation lies in its predictive ability. Currently, a significant distinction between the diffusive and displacive theories is that only the latter has been applied to alloy design.

An early area of interest was rail steels. Historically, rail steels have been pearlitic, however the presence of brittle carbides makes them vulnerable to fracture [117]. An demand for high-strength wear-resistant rails led many to consider a bainitic alternative, although early attempts produced alloys that did not perform as

well as the conventional steels [145]. The challenge was to develop a carbide-free steel consisting of bainitic ferrite and retained austenite: the difficulty was that suppressing cementite precipitation produced regions of blocky austenite that would transform to martensite under stress. By alloying appropriately, it is possible to alter the T_0' curve to encourage the bainite reaction to go further to completion, eliminating the blocky austenite. The bainitic alloys produced by this method outperformed pearlitic premium rail in both wear resistance and rolling contact fatigue life [117, 145].

A more recent innovation involved the design of carbide-free bainitic alloys for defence applications. The aim was to use the displacive theory to design alloys with "unprecedented combinations of strength and toughness in bulk samples" [135]. Upon testing, these alloys were found to display the then highest ever combination of strength and toughness seen in bainitic steel (1600 MPa, 130 MPa m$^{\frac{1}{2}}$) [136]. Development of this concept has led to the production of a range of high-strength bainitic steels with a nanoscaled structure [137, 138, 139, 146, 147, 148]. The properties exhibited by these steels match, and in some cases, exceed, those of other high-performance classes of steels, including TRIP-assisted steels, quenched and tempered martensitic steels, dual phase steels and maraging steels [146, 148, 149] (see Figure 12). The theory has also been used to modify the kinetics of the transformation in order to achieve more rapid transformation times [150, 151], and to enable transformation at lower temperatures [139]. Currently, however, the necessarily high carbon contents of these alloys precludes them from applications where weldability is important, limiting their scope.

The displacive theory has been used to design new alloys for a range of potential applications: aerospace; pipelines [152, 153]; bearings [154] — with promising results. Many of these areas are traditionally the preserve of quenched and tempered martensitic steels (favoured for their combined strength and toughness).

Casting a wider net, it is possible to find many other alloys which, while not specifically designed using a quantitative theory for bainite transformation, do owe their existence to the search for a more complete understanding of the bainite transformation. In the 1950s, for example, Irvine and Pickering worked on the development of low-carbon bainitic steels by applying their knowledge of hardenability to study the behaviour of a range of low-carbon alloys under various conditions of composition and heat treatment [155]. Their 'Fortiweld' steels have been described as the origin for all ultra-low-carbon bainitic steels in use today [156].
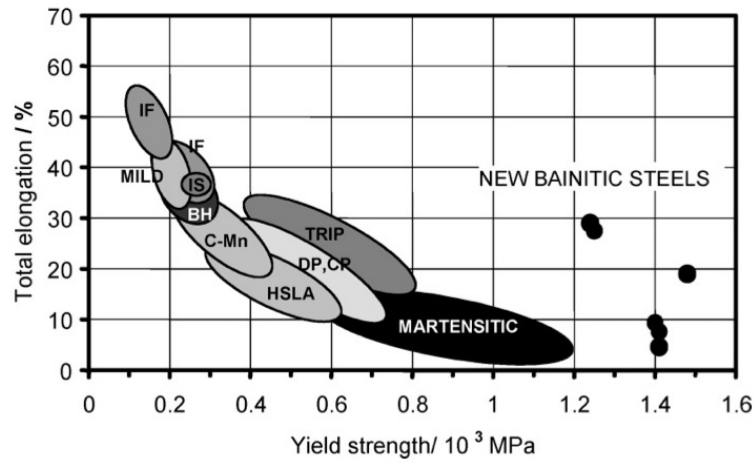
Figure 12: A comparison of elongation and strength of nanostructured bainite and conventional steels including: interstitial free (IF); carbon-manganese (CMn), bake hardenable (BH); isotropic (IS); dual phase (DP); complex phase (CP) [149]

TRIP steels, a more familiar class of alloys, were first developed back in the 1960s as part of an effort to better study the mechanism of bainite transformation [157]. In this application, the retained austenite resulting from the incomplete bainite transformation is crucial to achieving the mechanical properties. An adaptation of the carbide-free bainite structure led to the creation of TRIP-assisted steels, which rely on the composite nature of a mixed bainite-austenite-allotriomorphic ferrite microstructure to enhance their ductility [158]. The principle has recently been further expanded to produce TWIP steels, which claim greater elongation than TRIP and TRIP-assisted steels, and which have found applications in impact-absorbing vehicle structures [159].

11   Conclusions

The bainite controversy has persisted for eighty years. Described as "one of the [most] intensely discussed phenomena in steels" [100], it draws attention to the unusual and fascinating features of the bainitic microstructure.

The opposing theories of diffusion-driven transformation and diffusionless transformation both claim evidence in their favour. The problem, as both sides agree, is that "direct experimental evidence for either theories is difficult to obtain. Therefore, one is left with indirect evidence" [130]. Often the same evidence can be interpreted in the context of both mechanisms [2, 43] and for the undecided, it can be a challenge to establish which is the more convincing interpretation.

Summary Of The Theories

Diffusive

Bainite both nucleates and grows via a reconstructive mechanism. The growth rate is greater in the edgewise direction: lengthening of subunits dominates over thickening. This results in the formation and propagation of ledges. Cementite and ferrite grow simultaneously and cooperatively. Supporting evidence includes the metallographic similarities between bainite and other structures known to form via diffusion [25]; high resolution measurements of slow and continuous growth rates [2, 66]; and AFM measurements of a subunit showing a surface relief characteristic of a ledge mechanism.

The quantitative diffusive theory is able to calculate the limits of growth of both Widmanstätten ferrite and bainitic ferrite (in terms of a critical carbon content of austenite) [78]. It can also predict with reasonable accuracy the growth kinetics of bainite [124, 130, 131]. A limitation of the theory is an inability to account quantitatively for the effects of carbide-forming alloy elements, although it is thought that solute-drag may provide an explanation.

Displacive

A subunit of bainitic ferrite nucleates with carbon partitioning, and grows displacively until growth is halted by plastic relaxation in the adjacent austenite. Carbon is then rejected from the supersaturated ferrite by

diffusion and precipitation into the austenite (forming upper bainite) and may also precipitate within the subunit (forming lower bainite). New subunits nucleate and grow on the tips of old subunits. Where carbide precipitation is suppressed, bainite growth is limited by the T_0' curve resulting in incomplete transformation.

This theory is supported by measurements showing surface relief and plastic relaxation in the austenite [66, 118, 144]; measurements of high subunit growth rates [95]; X-ray measurements showing that retained austenite contents match the T_0' curve [9, 138, 144]; synchrotron studies showing carbon partitioning during nucleation [142]; and high resolution atom probe measurements of the carbon supersaturation in bainitic ferrite during transformation [143, 144].

The displacive theory explains why it is possible in high carbon steels to avoid the formation of upper bainite, and in low carbon steels to avoid forming lower bainite [106]. It accounts for a lack of partitioning of substitutional solutes and explains why Widmanstätten ferrite does not always form in steels, and why some steels only transform to martensite [71]. In its quantitative form, it is able to predict the shapes of TTT and CCT curves with reasonable accuracy [85]. It has been used to design many new bainitic alloys with excellent properties [117, 135, 136, 152, 154].

11.1   The Definitions of Bainite

It has become clear through the course of this review that a major challenge for researchers in this area is the conflict between the three major definitions of bainite. The generalised microstructural definition states that bainite is a nonlamellar eutectoid decomposition product [15, 16]. It has also been stated more specifically as describing "the product of the diffusional, noncooperative, competitive ledgewise growth of two precipitate phases formed during eutectoid decomposition, with the minority phase appearing in nonlamellar form" [160]. The surface relief definition describes bainite as a plate-shaped product that produces an invariant plane strain surface relief as formed by shear [43, 61]. The overall reaction kinetics definition incorporates the existence of an upper limiting temperature well below the eutectoid temperature (B_S) and an incomplete reaction phenomenon, and considers bainite to have a separate C-curve on a TTT diagram [26, 36].

These three definitions cannot simultaneously be true. Two of the definitions include a stated mechanism

of formation as part of the definition! It is then straightforward to dismiss any bainite-like structure that does *not* form via the expected mechanism as 'not bainite'. When faced with a huge quantity of literature on the subject of the bainite transformation, a lack of definitional consistency only serves to confuse the matter further. Indeed, a great deal of effort has gone into attempting to resolve this problem [160]. It is not trivial. It is, however, apparent that until a general consensus is reached as to the definition of bainite, it is unlikely that a similar consensus will be reached with regard to the mechanism of transformation.

<div align="center">***</div>

In the view of the author, the preponderance of scientific evidence is in favour of a displacive theory of transformation. Others may take a different view, however the value of the displacive theory in the design of new and effective alloys is hard to deny. Although a predictive ability alone does not imply that the fundamental science is explained (consider neural networks), in this case the theory also provides explanations for many observations, placing them within a single framework based upon solid scientific principles.

The evidence provided by the diffusional paradigm is not necessarily weaker, or incorrect, however. The proponents of the diffusional theory present good, convincing work, however it may not be accepted by others because of a fundamental disagreement as to which definition of bainite is correct. The diffusional theory should therefore not be discounted.

Acknowledgements

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