Bainite in Steels

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The mechanism of the bainite transformation in steels is reviewed, beginning with a summary of the early research and finishing with an assessment of the transformation in the context of the other reactions which occur as austenite is cooled to temperatures where it is no longer the stable phase. The review includes a detailed account of the microstructure, chemistry, and crystallography of bainitic ferrite and of the variety of carbide precipitation reactions associated with the bainite transformation. This is followed by an assessment of the thermodynamic and kinetic characteristics of the reaction and by a consideration of the reverse transformation from bainite to austenite. It is argued that there are useful mechanistic distinctions to be made between the coherent growth of ferrite initially supersaturated with carbon (bainite), coherent growth of Widmanstätten ferrite under paraequilibrium conditions, and incoherent growth of ferrite under local equilibrium or paraequilibrium conditions. The nature of the so-called acicular ferrite is also discussed.

I. INTRODUCTION

A. *The Discovery of Bainite*

DURING the late 1920's, in the course of some pioneering studies on the *isothermal* transformation of austenite at temperatures above that at which martensite first forms, but below that at which fine pearlite is found, Davenport and Bain[1] discovered a new microstructure consisting of an "acicular, dark etching aggregate," which was quite unlike the pearlite or martensite observed in the same steel. They originally called this microstructure "martensite-troostite," since they believed that it "forms much in the manner of martensite but is subsequently more or less tempered and succeeds in precipitating carbon."

The structure was found to etch more rapidly than martensite but less so than troostite (fine pearlite). The appearance of "low-range" martensite-troostite (formed at temperatures just above M_s) was found to be somewhat different from the "high-range" martensite-troostite formed at higher temperatures. The microstructure exhibited unusual and promising properties; it was found to be "tougher for the same hardness than tempered martensite"[2] and was the cause of much excitement at the newly established United States Steel Corporation Laboratory in New Jersey. In 1934, the research staff of the laboratory named the microstructure "Bainite" in honor of their colleague E.C. Bain, who had inspired the studies, and presented him with the first ever photomicrograph of bainite, taken at a magnification of 1000 times.[3,4]

The name "bainite" did not immediately catch on. It was used rather modestly even by Bain and his coworkers. In a paper on the nomenclature of transformation products in steels, Vilella *et al.*[5] mentioned an "unnamed, dark etching, acicular aggregate somewhat similar to martensite" when referring to bainite. Hoyt, in his discussion to this paper, appealed to the authors to name the structure, since it had been first produced and observed in their laboratory. Davenport[6] ambiguously referred to the structure, sometimes calling it "a rapid etching acicular structure," at other times calling it bainite. In 1940, Greninger and Troiano used the term "Austempering Structures" instead of bainite.[7] The 1942 edition of the book *The Structure of Steel*, and its reprinted version of 1947, by Gregory and Simmons, contains no mention of bainite.[8]

The high-range and low-range variants of bainite were later called "upper bainite" and "lower bainite," respectively,[9] and this terminology remains useful to this day. Smith and Mehl[10] also used the term "feathery bainite" for upper bainite, which forms largely, if not exclusively, at the austenite grain boundaries in the form of bundles of plates and only at high reaction temperatures, but this description has not found frequent use. In fact, both upper and lower bainite ferrite consist of aggregates of plates, and such aggregates were later designated as sheaves of bainite.[11]

B. *The Early Research*

Early research into the nature of bainite continued to emphasize its similarity with martensite. Bainite was believed to form with a supersaturation of carbon.[12–16] Vilella *et al.*[5] postulated that the transformation involves the abrupt formation of flat plates of supersaturated ferrite along certain crystallographic planes of the austenite grain; the ferrite then was supposed to reject carbon at a rate depending on temperature, leading to the formation of carbide particles (as opposed to the lamellar carbides found in pearlite). The transformation was believed to be, in essence, martensitic, "even though the temperature be such as to limit the actual life of the quasi-martensite to millionths of a second." Bain[2] reiterated this view in his classic book *Alloying Elements in Steel*. Isothermal transformation studies were, by then,

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becoming very popular and led to a steady accumulation of data on the bainite reaction (still variously referred to as the "intermediate transformation," "dark etching acicular constituent," "acicular ferrite," *etc.*).

For alloys of appropriate composition, the upper ranges of bainite formation were found to overlap with those of pearlite, preceded in some cases by proeutectoid ferrite. Thus, the nomenclature became further confused since the ferrite which formed first was variously described as massive ferrite, grain-boundary ferrite, acicular ferrite, Widmanstätten ferrite, *etc.* On a later view, some of these microconstituents are formed by a "displacive"[17] or "military"[18] transformation of the iron atoms (together with any substitutional solute atoms) from austenite to ferrite, and are thus similar to carbon-free bainitic ferrite, whereas others form by a "reconstructive" or "civilian" transformation, which is a quite different kinetic process.

1. *Crystallography*

By measuring the crystallographic orientation of austenite using twin vestiges and light microscopy, Greninger and Troiano[7] were able to show that the habit plane of martensite in steels is irrational; these results were consistent with earlier work on nonferrous martensites and disproved the contemporary view that martensite in steels forms on the octahedral planes of austenite. They also found that with one exception, the habit plane of bainite is irrational and different from that of martensite in the same steel. The habit plane indices also tended to vary with the transformation temperature and the average carbon concentration of the steel. The results seemed to imply some fundamental difference between bainite and martensite. Because the habit plane of bainite seemed to approach the austenite octahedral plane (then thought to be the habit plane of Widmanstätten ferrite) at high temperatures but the cementite habit at low temperatures, and because it always differed from that of martensite, Greninger and Troiano proposed that from the very beginning, bainite forms from austenite as an aggregate of ferrite and cementite. Thus, a competition between the ferrite and cementite of the aggregate was suggested as the reason for the observed variation of bainite habit, the ferrite controlling at high temperatures and the cementite at low temperatures. The crystallographic results were later confirmed by Smith and Mehl[10] using an indirect and less accurate method. These authors also showed that the orientation relationship between bainitic ferrite and austenite does not change very rapidly with transformation temperature and carbon concentration, and is within a few degrees of the orientations found for martensite or Widmanstätten ferrite, but differs considerably from that of pearlitic ferrite/austenite. Since the orientation relationship of bainite with austenite was not found to change, Smith and Mehl considered Greninger and Troiano's explanation for habit plane variation to be inadequate, implying that the habit plane cannot vary independently of orientation relationship.

2. *The incomplete-reaction phenomenon*

It was known as long ago as 1939 that in certain alloy steels (such as Fe-1.1Cr-1.1Mo-0.33C wt pct) "in which the pearlite change is very slow," the degree of transformation to bainite decreases (ultimately to zero) with increasing isothermal transformation temperature.[19] Similarly, the bainite transformation in an Fe-2.98Cr-0.2Mn-0.38C wt pct alloy was found to begin rapidly but cease shortly afterward, with the maximum volume fraction of bainite obtained increasing with decreasing transformation temperature.[20] At no temperature investigated did the complete transformation of austenite occur solely by decomposition to bainite. The residual austenite remaining untransformed after the cessation of the bainite reaction reacted by another mechanism (pearlite) only after a further long delay. Other experiments on several chromium-containing steels (0.08-1.28C wt pct) revealed that the total dilatometric expansion accompanying the initial rapid formation of bainite increased continuously with decreasing reaction temperature.[21] The curve of total expansion *vs* temperature was found to show an increasing slope as a function of carbon concentration. The odd feature of such results was that the bainite transformation did not seem to reach completion on isothermal heat treatment, even though full transformation to pearlite could be achieved at a *higher* transformation temperature. Often, the transformation of austenite at lower temperatures occurred in two stages,[20] beginning with the bainite reaction, which stopped prematurely, followed by the formation of pearlite at a slower rate. As will become apparent later, it is significant that the two reactions may only be separated by a long delay in well-alloyed steels; in plain carbon steels, "the second reaction sets in within a few seconds after the beginning of the bainite reaction."[20]

3. *Carbon redistribution*

X-ray and other experiments indicated that the formation of bainite enriches the residual austenite in carbon. Klier and Lyman[20] took this to imply that the austenite, prior to its transformation to bainite, becomes compositionally unstable and separates into carbon-rich and carbon-depleted volumes (a process like this would require uphill diffusion). The low-carbon regions were postulated to transform into supersaturated bainite of the same composition by a "martensite-like" lattice rearrangement, which then rapidly decomposed further by precipitating iron carbides. A similar suggestion had been made earlier by Kurdjumov[22] with respect to Widmanstätten ferrite: "regions of low carbon concentration in the γ crystal result from diffusion within the γ phase, and these regions can at this time transform into the α phase . . ."

4. *Thermodynamics*

In a far-reaching paper, Zener[23] attempted to give a rational thermodynamic description of the phase transformations that occur in steels. He assumed that bainite growth is diffusionless, any carbon supersaturation in bainitic ferrite being relieved subsequent to growth by partitioning into the residual austenite. The atomic *mechanism* of bainite growth was not discussed in detail, but he believed that unlike martensite, there is no strain energy associated with the growth of bainite. Thus, bainite should form by diffusionless transformation at a temperature just below T_o, where the austenite and ferrite of the same composition have identical free energy. However, T_o is frequently used in martensite theory for the temperature at which austenite and martensite (*i.e.*, supersaturated tetragonal "ferrite") have the same free energy; for clarity, we follow Christian and Edmonds[24] and call this temperature T_{om}. The Bain strain applied to a random interstitial solution of carbon in austenite automatically produces the ordered tetragonal form of ferrite if the carbon atoms are trapped in their original sites, but Zener also supposed that the tetragonal form may be regarded as a result of an ordering of the interstitial atoms into one set of sites of the cubic structure. He derived an equation for the critical temperature, T_c, at which the cubic and tetragonal forms of ferrite have the same free energy; T_c rises with interstitial solute content and, thus, intersects the M_s temperature and also has a joint intersection with the T_o and T_{om} temperatures. Clearly, T_{om} lies below T_o at low-carbon contents and above T_o at high-carbon contents. According to one interpretation,[25] martensite formed above room temperature is cubic at carbon contents below the intersection of M_s and T_c (above 2.5 at. pct carbon in plain iron-carbon alloys) and tetragonal above it. As Zener pointed out, martensite cannot form until the driving force obtained by supercooling below the T_o or T_{om} temperature is large enough to provide the necessary strain energy.

It is usually assumed that bainite forming first as fully supersaturated ferrite nevertheless has a cubic structure, but it would seem more logical to assume a tetragonal structure, unless the temperature of formation is above T_c.

The Zener model failed to provide an explanation of why the strain energy should exist for martensite and not for bainite. On the other hand, it explained the data showing that the degree of transformation to bainite increases with supercooling from zero at an upper limit, which is generally known as the B_s temperature. The carbon that partitions into the austenite *after* the formation of bainite changes its composition, until it eventually becomes thermodynamically impossible for the austenite to transform without a composition change. For a given alloy composition, a higher undercooling below T_o would allow more bainite to form before transformation without a composition change becomes impossible. Consistent with experimental data, the model also requires the bainite "*C*" curve of the time-temperature-transformation (TTT) diagram to tend asymptotically to infinite time at a temperature corresponding to T_o or T_{om}, whichever is the higher, since the transformation of austenite without a composition change cannot occur above this limit.

The initial plates of bainite, unlike those of many martensites, often grow to a limited size, less than that of the parent austenite grain. Zener postulated that this is due to the formation of a layer of cementite around the plate, which stifles any subsequent growth.

5. *Paraequilibrium*

By 1947, it was evident that the cementite, which grows during the bainite transformation in alloy steels, differed from that associated with pearlite. The pearlitic cementite was always found to contain a higher than average concentration of some substitutional alloying elements, whereas bainitic cementite seemed to have about the same overall substitutional alloy content as the parent material. Hultgren[26] has cited several references which report magnetic, chemical, and X-ray data on extracted carbides which confirm this difference between the two kinds of carbides.

Hultgren was, at the time, proposing a model for the role of substitutional alloying elements in steels; at high temperatures where diffusion rates are reasonable, these elements can redistribute during transformation if equilibrium demands such redistribution. In these circumstances, the transformation was said to occur under "orthoequilibrium" conditions. This compares with "paraequilibrium" transformation, in which the substitutional alloying elements are unable to partition during the time scale of the experiment, although carbon, which is a fast diffusing interstitial element, redistributes between the phases and reaches equilibrium subject to this constraint.

The mechanism of pearlite formation was itself not clear in those days, but the transformation was believed to be initiated by the nucleation of cementite. It was suggested that bainite was instead initiated by the nucleation of ferrite.[9,10,27] Hultgren put these ideas together and postulated that the transformation at high temperatures (upper bainite) begins with the nucleation of ferrite of paraequilibrium carbon concentration, so that the residual austenite is enriched with respect to carbon. This bainitic ferrite, unlike the ferrite associated with pearlite, was believed to have a Kurdjumov-Sachs (KS) or Nishiyama-Wasserman (NW) orientation relationship with the parent austenite in which it grows; this was considered to explain the difference in ferrite morphology observed experimentally in pearlite and bainite. Bainitic ferrite was always found to consist of individual plates or sheaves, whereas the ferrite in pearlite apparently formed alternating plates of a regularly spaced two-phase lamellar aggregate. The enrichment of austenite with respect to carbon should then eventually lead to the paraequilibrium precipitation of cementite from austenite in a region adjacent to the bainitic ferrite. At the time, pearlitic cementite was thought to bear a rational orientation relation to the austenite grain into which the pearlite colony grows, and Hultgren proposed, without any evidence, that bainitic cementite should be randomly oriented to the austenite in which it precipitated. This process of ferrite and subsequent cementite precipitation then repeated, giving rise to the sheaf of bainite. Therefore, Hultgren considered upper bainite to be a kind of a reconstructive transformation, in essence similar to pearlite but growing under paraequilibrium conditions and different in the orientation relations of the various phases with respect to the parent austenite.

No explanation was offered for the occurrence of paraequilibrium with bainite, nor for the existence of the various orientation relationships. He admitted the possibility that bainite formed at lower temperatures (later known as *lower* bainite) "forms directly," implying that the bainitic ferrite formed with a supersaturation of carbon, although the mechanism was not discussed.

The model of pearlite formation involving the repeated formation of ferrite and cementite was abandoned when Hillert[28] demonstrated that a pearlite colony really consists of two interwoven crystals, one of ferrite and the other cementite. Hillert[28,29] also pointed out an important distinction between pearlite and upper bainite; in the former case, the ferrite and cementite phases grow cooperatively, whereas in the latter case, the plates of bainitic ferrite form first, with the precipitation of cementite being a subsequent reaction.

6. *Kinetics*

The experiments of Wiester,[30] Hannemann *et al.*,[31] and Forster and Scheil[32,33] indicated that martensite can grow very rapidly in steels, with a plate taking a few microseconds to grow right across an austenite grain. Bunshah and Mehl[34] later demonstrated that the rate of growth of martensite can be as high as 1 km s^{-1}, *i.e.*, one-third the velocity of sound. This gave rise to the incorrect impression that martensitic transformation does not involve a "nucleation and growth process;" *i.e.*, it is not a first-order transformation in the thermodynamic sense.* For example, Smith and Mehl[10] wondered whether bainitic structures form by a process of nucleation and growth or whether the plates spring fully formed from the matrix lattice "as they do in the transformation to martensite." A nucleation and growth model was favored, since the sizes of the reacted regions apparently increased with time at the reaction temperature. This was consistent with the work of Wever and his coworkers,[12,13,36] who found that in the bainite transformation range, the austenite decomposes relatively slowly. Furthermore, the progress of the bainite transformation could be represented by means of a *C* curve on a TTT diagram,[1] with a well-defined incubation period before the beginning of isothermal transformation. Martensitic transformation, on the other hand, could not be suppressed by the fastest available quench rates;[37] it seemed to form athermally and was represented on the TTT diagram by a family of lines parallel to the time axis.[38] The bainite reaction was found to follow *C*-curve kinetics even below the M_s temperature.[39]

It is in this context that Ko and Cottrell[40] attempted to investigate whether bainite is "a nucleation and growth reaction, or like martensite, forms in a fraction of a second." They also wanted to establish whether the transformation leads to surface relief effects similar to those associated with martensitic transformations. Ko and Cottrell were able to demonstrate, through hot-stage light microscopy, that bainite grows relatively slowly and that its formation causes the shape of the transformed region to change, the shape change being characterized qualitatively as an invariant-plane strain. They also noted that unlike pearlite, which is not hindered by austenite grain boundaries,[27] bainite growth terminated at austenite twin or grain boundaries. Therefore, the transformation was similar to martensite, and Ko and Cottrell attempted to identify any clear differences that may exist between martensite and bainite.

It was known already that martensite first forms at a large undercooling below the T_o temperature, at which ferrite and austenite of identical composition have equal free energy.[23,41] Since diffusionless transformation is *thermodynamically* feasible below T_o, the extra undercooling was believed necessary to account for the strain and, to a lesser extent, the interface energy associated with the formation of the martensite plate. Bainite, which can form at more elevated temperatures than martensite, should, therefore, require a modified mechanism of transformation, a mechanism which has to be consistent with the lower driving force that is available for the transformation of austenite at higher temperatures. Ko and Cottrell postulated that a "coherent nucleus" can develop either into martensite or into bainite, depending on the driving force available for transformation, the nucleus developing into martensite below M_s. At the higher temperatures where bainite occurs, "coherent growth" can only "take place when the strain due to the density change is relieved." They suggested that this could happen if the amount of carbon dissolved in bainite is reduced; this would also lead to a free energy reduction. The removal of carbon from the ferrite could occur by diffusion from bainite or by precipitation within bainite, or by a combination of these processes, depending on the transformation temperature. It is not entirely clear from their description whether they envisaged initially diffusionless growth followed by carbon diffusion to provide the driving force for further growth, or whether the diffusion and interface migration are coupled so that precipitation within the ferrite (for lower bainite) or carbon rejection to the austenite (for upper bainite) takes place at the moving interface. The former mechanism seems illogical, since the extra driving force is only available after a stage of initial growth to martensite, which should not be possible (according to their growth condition) above M_s. Provided there is some way of circumventing the difficulty of forming the initial coherent nucleus (of whatever composition), the second type of growth model would allow bainite to form above M_s and, indeed, above T_o. In some later work, Ko[42] distinguished between incoherent ferrite and "acicular ferrite," which he proposed should be regarded as carbon-free bainitic ferrite.

Kriesement and Wever[43] pointed out that the appearance of bainite changes continuously between upper and lower bainite and postulated that the growth of bainite involves the repeated and alternating nucleation and growth of lamellae of cementite and ferrite from austenite; unlike pearlite, the growth direction of the macroscopic plate of bainite was supposed to be normal to the plane of the lamellae. Although this particular mechanism has since been shown to be incorrect, they identified clearly the condition necessary for cementite precipitation to occur from residual austenite during the bainite transformation. Cementite (θ) precipitates from austenite if the carbon concentration of the latter exceeds that given by the extrapolated $\gamma/(\gamma + \theta)$ phase boundary.

Although many of the characteristics of bainite,

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*The Ehrenfest[35] classification of phase transformations 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 a first-order transformation, the partial derivative of the Gibbs free energy with respect to temperature is discontinuous at the transition temperature. Thus, there is a latent heat of transformation evolved at a sharp transformation interface which separates the coexisting parent and product phases. The phase change occurs at a well-defined interface, the interface separating perfect forms of the parent and product phases. First-order transformations involve the nucleation and growth of a product phase from the parent phase. In a second-order transformation, the parent and product phases do not coexist. Martensite in steels can coexist with austenite and is then separated from the latter by a well-defined interface. It is, like bainite, a first-order transformation involving the nucleation and growth of individual plates.

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.[44] He used the Dubé morphological classification[45,46] for all nonpearlitic 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 a later discussion of bainite,[47] he developed the "microstructural" definition, in which bainite is regarded simply as a nonlamellar two-phase aggregate of ferrite and carbides in which the phases form consecutively (as distinct from pearlite, where they form cooperatively). Aaronson stated that according to this definition, the upper limiting temperature of bainite formation should be that of the eutectoidal reaction ($Ae1$), 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 formation (B_s) were attributed to a special effect of certain alloying elements on the growth kinetics. Aaronson equally dismissed the observation of surface relief as a basis for classifying the various forms of ferrite.

C. *Summary of the Early Research*

By the beginning of the 1960's, bainite was generally regarded as a transformation product differing significantly from various forms of proeutectoid ferrite, as well as from pearlite and martensite. The results of the early research can be summarized as follows.

Bainite can be obtained by isothermal transformation at all temperatures where the formation of pearlite and proeutectoid ferrite is sluggish and also at temperatures below the martensite-start temperature.

Upper bainite, when it forms at relatively high temperatures, was found to consist of sheaves of ferrite plates with cementite particles trapped between the plates, whereas lower bainite contained fine cementite particles within the bainitic ferrite platelets themselves.

Observations using light microscopy indicated that the lengthening of bainite sheaves occurred at a rate much slower than that at which martensite plates were known to grow. Bainite sheaves were found to have irrational habit planes, the indices of which differed from those of martensite found in the same alloy. The orientation relationship between bainitic ferrite and austenite was, on the other hand, similar to that between martensite and austenite. Bainite plates were never found to cross austenite grain boundaries, and the formation of bainite was, like martensite, observed to cause the shape of the parent crystal to change. This shape deformation amounted, in present day terminology, to an invariant-plane strain (IPS).

In steels where transformation to bainite could be carried out without interference from other reactions, experiments demonstrated that the degree of transformation to bainite decreases (ultimately to zero), and the time taken to initiate the reaction increases rapidly with increasing isothermal transformation temperature. This led to the definition of a "bainitic-start" temperature, B_s, above which there is no reaction; this temperature was always found to lie well within the (metastable) $\alpha + \gamma$ phase field. Other reactions could follow the bainitic transformation, but in all cases, the rapid formation of bainite ceased prematurely before the austenite was fully transformed.

The prevailing, albeit rather ill-defined, concept of the bainite reaction as involving a martensitic-type interface combined with diffusion-controlled growth had already led to the suggestion of bainitic reactions in other (nonferrous) alloy systems. In particular, the observation of surface relief effects apparently combined with compositional changes in the decomposition of some β-phase copper-zinc alloys had been used in a pioneering paper by Garwood[48] to identify this decomposition as bainitic, and the difficulties in accounting for such a reaction in purely substitutional alloys had been emphasized.[49] This remains an interesting and controversial aspect of transformation theory.[50,51]

In summary, the early emphasis on the similarities between bainitic and martensitic transformations still dominated the literature in the 1960's, and the contrasting views of Aaronson and his co-workers were only beginning to emerge. These views, however, later led to considerable controversy, which has continued until the present time. Some of the dispute has been only semantic and, thus, of marginal importance; into this category, we would put Ko's proposal that the term "bainite" should be extended to include Widmanstätten ferrite forming with a shape change (thus satisfying what Aaronson has termed the shear definition of bainite, but contravening the reaction kinetics definition). The various disputes do, however, also concern mechanisms and, thus, are important. In what follows, we shall be arguing that there are useful mechanistic distinctions to be made between the coherent growth of ferrite initially supersaturated with carbon (bainite), the coherent growth of Widmanstätten ferrite under paraequilibrium conditions, and the incoherent growth of ferrite under local equilibrium conditions.

II. BAINITIC FERRITE

In this section, we propose to discuss in detail the ferritic component of bainite, focusing on its morphology, crystallography, constitution, and kinetics. The treatment of the carbides associated with the bainite transformation is discussed in Section III.

A. *Sheaves of Bainite*

1. *Morphology*

Both upper and lower bainite consist of aggregates of platelets or laths of ferrite separated by regions of *residual* phases. These consist of untransformed austenite or of phases such as martensite or cementite, which form subsequent to the growth of bainitic ferrite. The aggregates of bainitic platelets are called *sheaves*,[11] and the individual platelets are sometimes called *subunits*. The platelets within a given sheaf may not be completely isolated from one another by the residual phases, in which case, low-misorientation grain boundaries are formed along the surfaces where the platelets come in contact. This is because within a sheaf, the subunits all tend to be in a common crystallographic orientation. The cluster of platelets that form a sheaf is sometimes called a "packet" of bainite because, on the scale of light microscopy, fully transformed grains of austenite appear to be divided into discrete regions (*i.e.*, packets), within which the traces of the habit planes of bainite are parallel. The term has its origins in the description of lath martensite in low-alloy, low-carbon steels, where laths of martensite are also found to be in parallel formations (*e.g.*, References 52 and 53). The similarity in both morphology and crystallography between lath martensite and upper bainite has been noted in many investigations, but it also appears that there may be differences in the detailed crystallography (see Section II–D).

A possible explanation for the fact that some of the austenite adjacent to the bainitic ferrite remains untransformed at the reaction temperature is that its carbon concentration increases as a consequence of transformation to such an extent that the formation of bainite eventually becomes thermodynamically impossible. If the starting carbon concentration of the steel is large, the formation of bainite ceases at an earlier stage of the reaction, and the volume fraction of the residual phases is then expected to be large.

Two-surface analysis and other observations on specimens partly transformed to bainite show that the overall morphology of a sheaf on a macroscopic scale is in three dimensions, like that of a wedge-shaped plate, the thicker end of which originates at an austenite grain boundary.[54–59] The microscopic subunits, within a sheaf themselves, have a lenticular plate or lath morphology which is most prominent near the edge or tip of a sheaf where impingement effects are minimal; for the same reason, these features are easily observed in partially transformed specimens. The width of a subunit near the tip of a sheaf is approximately the same as that near the original nucleation site of the sheaf (*i.e.*, an austenite grain surface), implying that the subunits grow to a limiting size. In the development of a sheaf, new subunits are most frequently nucleated near the tips of subunits, which are already present, rather than on their sides. The overall morphology of a sheaf is illustrated schematically in Figure 1.

When the subunits are in the form of laths, each lath has its longest dimension along the close-packed direction of the ferrite, which is most nearly parallel to a close-packed direction of the parent austenite.[60] It is not clear why the subunits sometimes grow in the form of laths,[54,60,61] whereas on other occasions form as plates.[54,56,57,59,62] A qualitative impression from the literature is that the plate morphology tends to form at lower transformation temperatures.

In some cases, lower bainite sheaves seem to develop with a macroscopically planar interface on just one side of each sheaf;[57,63] the same effect has been found in lath martensite in an iron-nickel-manganese alloy.[64] In other cases, the thickening of sheaves has been observed to occur from both sides of the habit plane.[65] The aspect ratio (thickness/length) of such sheaves is known to decrease with transformation temperature but is not sensitive to the substitutional alloy content, at least for the relatively low-alloy steels that have been studied to date.[65,66,67] The sheaf width decreases with transformation temperature,[68,69] although the subunit width is not influenced by either the austenite grain size or the bainite sheaf size.[69,70] Similar effects are found with martensite,[71,72] but their detailed explanation is not yet available.

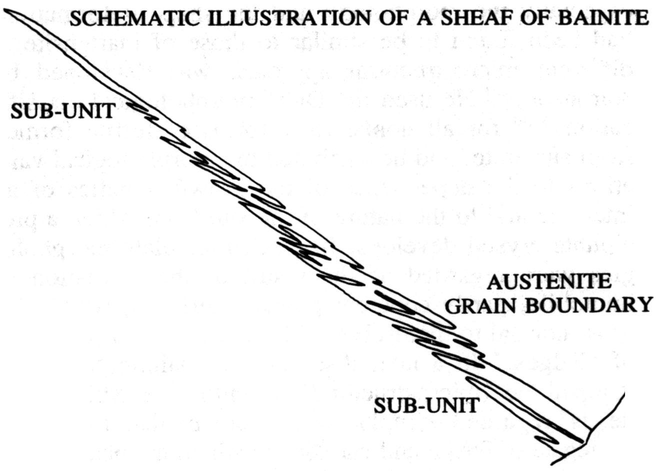

Fig. 1 Schematic illustration of the morphology of a sheaf.

2. *Stereology*

The "grain size" of bainite usually has to be characterized by measurements made on *random* planar sections of the microstructure, as observed using a transmission electron microscope using replica or thin foil specimens. In such sections, the ferrite plates appear approximately parallel-sided, and the thickness is then measured in a direction normal to the long edges of the plates. The average value of the measurements is taken to represent a "grain size," which is really an apparent plate thickness. The procedure is useful in characterizing any qualitative trends in microstructure but obviously ignores stereological considerations. For example, if a platelet is represented as a disc of radius, r, and thickness, t, with $r \gg t$, then the mean intercept length is given by $\bar{L}_3 = 2t$, and the mean intercept area is given by $\bar{A} = 2rt$.[73] Note that the intercepts are, in this case, random with respect to the orientation of the microstructure.

The specific manner in which the grain size of an anisotropic structure is defined is also application-dependent. For example, in considering strengthening due to lath boundaries, it is appropriate to examine the dimensions of the available slip planes within individual platelets.[74,75] If it is assumed that there is a random distribution of slip plane orientations with respect to the lath axes, the grain-boundary strengthening effect (σ_g) is found to be of the form $\sigma_g = k_g M^{-1}$, where k_g is a constant and M is the mean value of the larger diameter of a slip plane. Note that this behavior differs from the classical Hall-Petch relation, where it is the inverse square root of grain size which matters.

There is some uncertainty about the influence of carbon on the grain size of bainite; Pickering[76] found the size to be independent of carbon concentration for bainite produced during continuous cooling transformation, although Davenport[60] states (without citing evidence) that it is a well-known effect that the size decreases with carbon concentration. In fact, the apparent thickness of bainite is, in general, found to increase with transformation temperature from about 0.2 to 2 μm when the transformation temperature changes from 425 °C to 570 °C, respectively, for an Fe-0.22C wt pct commercial steel, and similar data have been reported for other steels.[77-80] Whether this reflects a change in the plate aspect ratio is not clear.

Bainitic ferrite formed at high temperatures often contains subgrain boundaries, the subgrain size becoming finer for bainite formed at lower temperatures.[76] The boundaries are probably a consequence of the recovery (polygonization) of the dislocation structure introduced during transformation at high homologous temperatures.

B. *Dislocation Density*

It is commonly observed in experiments using transmission electron microscopy (TEM) that bainite has a "high" dislocation density, although there are few quantitative data to support this. Smith[81] has shown, using TEM, that an Fe-0.07C-0.23Ti wt pct alloy, the estimated B_s temperature of which is about 650 °C,[82] has a mean dislocation density of 0.5×10^{14} m^{-2} when isothermally transformed to allotriomorphic ferrite at 800 °C, whereas when the same alloy is transformed to bainite at 650 °C, the dislocation density obtained is 4×10^{14} m^{-2}. It is particularly significant that the dislocation density in bainite is found to be higher than that in allotriomorphic ferrite, which has formed at a similar transformation temperature.[63]

The relatively high dislocation density associated with bainitic ferrite is often attributed to the fact that it forms by a shear mechanism, on the grounds that this necessitates the deformation of the parent lattice by dislocations which are then somehow incorporated into the product phase. This reasoning is, however, incorrect, since the dislocations that are responsible for the transformation and for the lattice-invariant deformation are located in the interface between the parent and product lattices. Indeed, there are many such transformations where few dislocations are to be found in the product phase (*e.g.*, thermoelastic martensites).

If the shape deformation accompanying displacive transformation is accommodated at least partially by plastic relaxation, then the resulting dislocation debris introduced into the austenite can be inherited by any bainite that forms subsequently. Plastic relaxation may also follow in the bainite itself, since the yield stresses of both ferrite and austenite decrease with increasing transformation temperature. Plastic relaxation of the shape change has been observed experimentally; when prepolished samples of austenite are transformed to bainite, the adjacent austenite surface does not remain planar but, instead, exhibits curvature which is characteristic of slip deformation.[57] Observations of the transformation using hot-stage TEM have revealed that the growth of bainite is accompanied by the formation of dislocations in and around the bainite,[83] and direct observations of the austenite/bainitic ferrite interface also provide evidence of plastic accommodation in both phases.[84] Sandvik and Nevalainen[80] have demonstrated that the austenite adjacent to the bainitic ferrite undergoes twinning deformation and that the density of twins increases as the transformation temperature decreases. The plastic accommodation is also believed to be responsible for the lower residual stresses in samples which are bainitic, compared with those transformed to martensite.[85]

The dislocation density of bainitic ferrite seems to increase as the transformation temperature is reduced,[86] although there are few quantitative data to this effect. X-ray line profile measurements show that the lattice strain (due to the presence of dislocations) increases as the transformation temperature decreases.[87] These can be used to estimate the dislocation density, ρ_d; for the low-alloy steel used by Fondekar *et al.*,[87] isothermal transformation to bainite at 300 °C, 360 °C, and 400 °C gave dislocation densities of 6.3×10^{15}, 4.7×10^{15}, and 4.1×10^{15} m^{-2}, respectively.

C. *Chemical Composition*

1. *Substitutional alloying elements*

It is generally accepted that there is no long-range redistribution of substitutional alloying elements during the growth of bainitic ferrite. See, for example, Aaronson and Domian,[88] where some of the electron-microprobe analysis results refer to bainitic ferrite. The bulk substitutional alloy content of the bainitic ferrite was found to be identical to that of the parent austenite. A variety of other results using the atom-probe technique on steels containing silicon, nickel, manganese, chromium, or molybdenum confirm that there is no bulk partitioning of substitutional alloying elements during the formation of bainitic ferrite.[89-93] One set of atom-probe experiments[94] apparently indicated the opposite conclusion, namely, that there is a redistribution of chromium and molybdenum during the formation of bainite. These results are, however, doubtful, since they indicate a depletion in the interface and an enrichment in the bulk phases on both sides of the transformation interface. Indeed, the measured concentrations in both phases sometimes exceeded the average concentration in the alloy used.

The behavior of the atoms on substitutional sites during transformation is critical in specifying the mechanism of the change. The iron and substitutional atoms (X) do not diffuse during displacive transformation, so that the ratio of Fe/X atoms is expected to be constant throughout a transforming crystal, even on the finest conceivable scale.

During reconstructive transformation, the atoms transfer across the interface in an uncoordinated manner which accomplishes the required lattice change and simultaneously ensures a minimization of the strain energy. This requires the thermally activated migration (in the interface region at least) of all the atoms, irrespective of whether the transformation occurs in a pure metal or in an alloy. There will normally be a volume change associated with the stress-free change of structure, and, at sufficiently high temperatures, this may be compensated by a flux of vacancies (and an opposite flux of atoms) between the growing precipitate and the dislocations, grain boundaries, and (ultimately) the free surface of the parent phase. At temperatures where the rate of diffusion in the parent phase is inadequate for such an adjustment, reconstructive growth with minimum strain energy will still be possible if the precipitate has a lenticular (tapered plate) shape, and the reconstruction takes place in such a way that the volume change is simply an expansion or contraction normal to the plane of the lens. This can be achieved by atomic migration entirely within, or in the limit around, the particle. Reconstructive growth is, however, scarcely feasible unless all atoms have some mobility in the incoherent interface, roughly equivalent during the time of growth to a diffusion distance of the order of magnitude of the dimensions of the particle. This necessary mass flow has been described as "reconstructive diffusion," and the two classes of transformation have been called "diffusional" and "displacive"[95] in place of the older divisions mentioned above, into "reconstructive" and "displacive" or "civilian" and "military." Bainite was one of the first transformations for which this wider classification was needed to replace the original division into "nucleation and growth" and "martensitic" transformations,[18,96] and we avoid using the term "diffusional transformation" here, since it refers only to the motion of the Fe + X atoms. If diffusional is used as one main category, there is the apparent paradox that a displacive transformation, in which there is segregation of carbon during growth, has to be described as "nondiffusional" even though the growth rate might be controlled by the diffusion rate of carbon!

In an alloy in which there is some atomic mobility within the parent phase, the reconstruction provides an opportunity for the solvent and solute atoms to redistribute between the two phases. However, in a system such as Fe-C-X, the diffusion rate of carbon in the austenite may be as much as 10^7 to 10^9 times greater than that of a substitutional atom in the temperature range of interest,[97] and these very different rates of atomic migration mean that true equilibrium segregation with regard to all components may not be produced at a migrating interface. It is, however, possible to envisage growth under diffusion control with local equilibrium at the interface in the sense that the compositions of the two phases are joined by a tie line of the equilibrium diagram, even though this tie line does not pass through the point representing the initial (or average) composition of the alloy. When these kinetic restrictions apply, the two phases may differ either significantly or negligibly in substitutional solute content. A qualitative analysis for ternary steels was first developed by Hillert,[98] and a simplified quantitative theory in which diffusion cross terms are neglected was developed by Kirkaldy,[99] Purdy *et al.*,[100] and Coates;[101] the effect of the cross terms was later examined by Coates.[102,103] The simple theory shows that for the diffusion-controlled growth of ferrite from austenite in an Fe-C-X alloy with initial composition near the $\gamma/\alpha + \gamma$ phase boundary (*i.e.*, with a small supersaturation), the tie line selected will have the carbon composition of the austenite at the interface almost equal to that of the bulk alloy so that the activity of carbon is nearly constant in the austenite, thus reducing the driving force for carbon diffusion almost to zero. There will be a concentration gradient of the substitutional solute ahead of the interface, resulting in appreciable partition, and the relatively slow growth rate will be determined by the diffusion rate of this solute. For large supersaturations, the tie line will have the Fe + X composition of the ferrite virtually identical with that of the bulk austenite and partitioning of the substitutional solute will be extremely small, with a relatively fast growth rate. These are referred to as the partitioning local equilibrium (P-LE) and negligible partitioning local equilibrium (NP-LE) growth modes,[100,102,103] and, for a high ratio of the diffusivities, the theory predicts an abrupt transition from one to the other as the supersaturation increases.

In the NP-LE mode, the concentration of X is uniform, except for a small "spike" in the parent phase adjacent to the interface. As the ratio of interstitial:substitutional diffusion rates increases, the width of this spike decreases, and when it becomes of the order of atomic dimensions, the concept of local equilibrium at the interface is invalid and has to be replaced (assuming the growth is, nevertheless, diffusion-controlled) by that of paraequilibrium.[98,104–107] In conditions of paraequilibrium, there is no redistribution of Fe + X atoms between the phases, the Fe/X ratio remaining uniform right up to the interface. One interpretation of the paraequilibrium limit is that reconstructive transformation occurs with all displacements of the Fe + X atoms taking place in the incoherent interface; another interpretation might be that only displacive transformation can occur. In either case, to quote from Coates, "the slow diffuser and the solvent participate only in the change of crystal structure." Paraequilibrium implies that the growth rate is controlled by the interstitial diffusivity, the interface compositions now being given by the tie lines of the pseudoequilibrium between the two phases under the constraint of a constant Fe-X ratio.

In conclusion, the experimental evidence that bainitic ferrite has the same bulk substitutional content as its parent austenite is consistent with both reconstructive and displacive mechanisms for the change in crystal structure. However, reconstructive transformation with local equilibrium (or, indeed, any state between local and paraequilibrium) 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,[89–93] have all 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. These experiments were all based on steels where other reactions do not interfere with the formation of bainitic ferrite. Measurements of the growth rates of grain-boundary allotriomorphs of ferrite from austenite in alloy steels under conditions where bulk segregation is not observed (*e.g.*, References 108 and 109) indicate calculated thicknesses of the spike of much less than 0.1 nm, and although these results are complicated by the effect of grain-boundary diffusion, they are in general agreement with the concept that the lattice diffusion rate is inadequate to sustain local equilibrium at the growing interface. Only at temperatures above 600 °C has segregation of some (though by no means all) substitutional elements been obtained in grain-boundary allotriomorphs.[88] Allotriomorphs are agreed to form by reconstructive mechanisms, but the absence of bulk segregation at moderately high transformation temperatures reinforces the belief, derived from the observed shape change, that bainitic ferrite forms at lower temperatures by a displacive rather than a reconstructive mechanism.

2. *Interstitial alloying elements*

A particular experimental difficulty with the bainite transformation is that in the case of upper bainite, at least, it is almost impossible to say anything about the initial carbon content of the ferrite because the time taken for any carbon to diffuse into austenite can be very small. For the moment, we refer to the interstitial content of bainitic ferrite *after* transformation. As will be seen later (Section IV), the concentration *during* transformation is likely to be different.

Internal friction experiments indicate that the amount of carbon which associates with dislocations in bainitic ferrite increases as the transformation temperature decreases, but it is independent of the alloy carbon concentration, at least in the range of 0.1 to 0.4 wt pct C.[86] This is consistent with the observation that the dislocation density of bainitic ferrite increases with a decrease in transformation temperature. The insensitivity to the alloy carbon concentration is because most of the carbon either ends up in the residual austenite or precipitates as carbides in the ferrite. The results also show that at some stage during the evolution of bainitic ferrite, it must have contained a higher than equilibrium concentration of carbon.

These observations have been confirmed directly by using microanalysis on an imaging atom probe, which has demonstrated quantitatively that the *post-transformation* carbon content of bainitic ferrite tends to be significantly higher than equilibrium.[89–93]

D. *Crystallography*

The properties of bainitic steels are believed to depend on the crystallographic texture that develops as a consequence of transformation from austenite. As an example, the ease with which slip deformation is transmitted across adjacent platelets of bainitic ferrite must be related to their relative orientation in space. Bainite grows in the form of clusters of platelets called sheaves, with little misorientation between the platelets within any given sheaf. Where they touch, adjacent platelets are separated by low-misorientation grain boundaries.

The relative orientation of the bainitic ferrite and its parent austenite is always close to the classic KS[110] and NW[111] relationships. These two rational relations differ only by a relative rotation of 5.25 deg about the normal to the parallel close-packed planes of the two structures, and the exact relative orientation in martensites is found to be intermediate and irrational, as is predicted by the crystallographic theory. High accuracy is required to compare theory with experiment, since the predicted orientation relation is insensitive to input parameters such as lattice spacings or lattice-invariant deformation. In the case of bainite, as in that of lath martensite, such precision is difficult to achieve, partly because of the experimental difficulties in retaining austenite and partly because of the high dislocation densities.

Despite these difficulties, it is significant that the experimental data always lie well within the "Bain region" which encompasses the KS and NW relationships. The Bain strain[112] is the pure part of the lattice deformation which, for displacive transformations in steels, converts austenite into ferrite or martensite. During the Bain strain, no plane or direction is rotated by more than 11 deg[113] so that any pair of corresponding planes or directions may be made parallel by utilizing a lattice deformation in which the Bain strain is combined with a rotation of not more than 11 deg. This defines the Bain region, and, for a displacive transformation, it is expected that the experimentally observed orientation relation will lie within this region. This need not be the case for reconstructive transformations, and allotriomorphic ferrite in steels is known to grow into austenite grains with which it has an orientation which is random or outside the Bain region.[114] Hence, it is very significant that bainitic ferrite always exhibits an orientation which is close to KS or NW and well within the Bain region.

Pickering[86] has suggested that the crystallography of bainite can be explained if the individual platelets or laths adopt different variants of the NW or KS orientations, such that the ferrite orientations within a sheaf can be generated simply by rotation about the normal to a specific close-packed plane of the austenite. In this way, the bainite laths may nucleate side-by-side in rapid succession with the transformation strains determining the variant. This early work was based on measurements only of ferrite-ferrite orientation relations, since the specimens may have contained only thin films of austenite which are observable only with high-resolution microscopy. However, it must be admitted that results from more recent work, in which measurements of the direct austenite-ferrite relations have been made, are still rather contradictory. There is general agreement that adjacent platelets or laths in bainite all have a $\{110\}_\alpha$ plane parallel (or almost parallel) to the same close-packed $\{111\}_\gamma$ and that the macroscopic habit plane is near to $\{111\}_\gamma$ in upper bainite but is irrational in lower bainite. Most investigators,[59,115] find all the platelets within a sheath or "subpacket" to have a common orientation, but Sarikaya *et al.*[116] claim that while some groups of adjacent laths have a common orientation, others have either different variants of the orientation relationship or, in lower bainite, are twin-related. Similar discrepancies exist in crystallographic measurements on lath martensite, where three types of orientation relation between adjacent laths of a packet are reported by some workers[116,117] and only one common orientation by others.[64,118]

When there is a common orientation, the platelets within a sheaf have small misorientations; there is also an appreciable spread of orientation within a single platelet because of its high dislocation density. Direct crystallographic analysis[115] indicates that all platelets within a subpacket have an irrational orientation relation with the austenite, which is rather closer to NW than to KS. Moreover, the shape deformations of all the platelets are identical in agreement with earlier work.[57,59] One further crystallographic observation made by Sandvik[115] is of considerable interest. He found that twins formed in the austenite adjacent to the ferrite and that the ferrite laths were able to grow through the twins, producing a reorientation of the lattice and also displacing the direction of the twin boundaries in the manner expected for a displacive (shear) transformation.

Similar results for the relative orientations of adjacent platelets were obtained in a careful examination of lath martensite by Sandvik and Wayman, using an iron-nickel-manganese alloy which contained appreciable retained austenite.[64] They found that although the laths had slight relative misorientations of up to 2 deg, they all exhibited the same variant of the parent-matrix orientation relation, and thick layers of austenite between adjacent laths indicated that the laths did not form as a result of self-accommodation of their shape strains. Thus, this form of lath martensite seems to be very similar, in substructure at least, to the bainite investigated by Sandvik.

One possible reason for a common orientation might be that the individual platelets of a sheaf are not separate crystals but are continuously connected portions of the growth front of one original nucleus. At the relatively high temperatures at which bainite (and lath martensite) form, the shape change may cause plastic deformation of the structure leading to copious generation of dislocations, which stops the forward growth of a platelet after it has attained a certain size. "Nucleation" of a new platelet would then simply be resumed growth caused by breakaway of a part of the original interface in a region near, but not at, the tip. In bainite, the growth would resume only after some carbon had been rejected from the ferrite into the austenite and would be most likely where pinning by dislocation debris is minimal and where the driving force is highest due to rapid dispersion of the carbon rejected to the austenite.

An alternative model is that the individual platelets are completely separated from each other by thin layers of austenite, so that each is separately nucleated but always in the same orientation. In general, the stress field at the tip will favor renucleation in the same variant, whereas that at the side of the platelet will favor another variant. The nucleation of other variants is, of course, essential if self-accommodating groups are to form and, thus, must be suppressed for some reason, perhaps because adjacent sheaves are formed together in a self-accommodating fashion. At present, there is insufficient evidence to determine whether either of these speculative descriptions is valid, although Srinivasan and Wayman,[56,57] Sandvik,[115] and Sandvik and Wayman[64] all claimed that the individual laths in their specimens were isolated from each other by retained austenite.

As already mentioned, early conclusions about mutual accommodation may have applied to sheaves rather than to platelets in each sheaf. Sandvik measured the misorientations between neighboring subpackets (presumably neighboring sheaves) in one "packet" of his bainitic alloy and found that these correspond to different variants of his irrational orientation relation in which the same austenite {111} plane is parallel to a ferrite {110} plane. The six variants which satisfy this condition lead to four different relative orientations, one of which is only 3 deg from the original orientation, and the others are, respectively, 8, 11, and 14 deg away from a twin orientation. Sandvik comments that the first misorientation is difficult to detect and that it is difficult to distinguish the remaining three from each other. He also comments that only the variant with orientation relation 14 deg from a twin relationship gives efficient self-accommodation, and this was observed fairly infrequently. Thus, adjacent subpackets are attributed to random association, although it is not clear why they should then all have the same pair of parallel close-packed planes. Sandvik and Nevalainen[80] have also suggested that adjacent sheaves of bainitic ferrite are approximately twin related and correspond to variants of a near NW orientation.

1. *Autocatalytic nucleation*

Autocatalytic nucleation is a term commonly associated with martensitic transformations.[119,120] The nucleation of martensite in steels is believed to begin at structural imperfections in the parent phase, such as arrays of dislocations. These are the preexisting defects which, on cooling below the M_s temperature, dissociate into suitable partial dislocations in a way which leads to the nucleation of martensite.[121,122,123] The defects are not all identical (they vary in potency) and are stimulated to grow into plates of martensite at different degrees of undercooling below the M_s temperature. This is the cause of the classical behavior observed for athermal martensitic reactions in which the volume fraction of martensite varies only with the undercooling below M_s.

Detailed analysis reveals that the initial number density of preexisting defects typically found in austenite is not large enough to explain the kinetics of martensitic transformation. The extra defects necessary to account for the faster than expected transformation rates are attributed to autocatalysis: when plates of martensite form, they induce new embryos which are then available for further transformation. Three mechanisms have been proposed for autocatalysis.[124] In stress-assisted nucleation, the activation of less potent defects at a given temperature is induced by the internally generated elastic stresses arising as a consequence of the shape change due to transformation. In strain-induced autocatalysis, the creation of new and more potent nucleating defects is induced by some plastic accommodation in the parent phase. Finally, "interfacial autocatalysis" refers to the nucleation of new martensitic units from the existing martensite/austenite interfaces. Autocatalysis is responsible for the "bursts" of transformation that occur in certain martensitic steels, from which the initial formation of a plate stimulates a disproportionately large degree of further transformation, sometimes causing the emission of audible clicks.

All of these effects arise as a consequence of the severe elastic and plastic disturbance of the austenite in the immediate vicinity of a plate of martensite. It is the shape change due to the martensitic transformation that is the cause of the disturbance. On this basis, autocatalysis should also feature prominently in bainitic transformations which are accompanied by similar shape deformations. There is, however, a significant difference in that bainite formation occurs at relatively low driving forces, where defects induced by transformation do not seem to play as crucial a role in stimulating further nucleation. The initial nucleation event is almost always confined to the austenite grain surfaces, which presumably contain the most potent defects for nucleation.

Intragranular nucleation of bainite can essentially be ignored except when nonmetallic particles may act as nucleation surfaces. The initial formation of a platelet of bainite (or of lath martensite) must lead to appreciable elastic and plastic strains, but this does not seem to cause the nucleation of other platelets in different orientations, as happens with plate martensite, and "bursts" of transformation are not observed. In the case of bainite, this may be because the driving force is only adequate for the formation of a carbon-free nucleus, and this may be impossible to form in the carbon-enriched region around an existing platelet. Whatever the reason, it seems that strain-induced autocatalysis does not play an important role in bainite formation. As already discussed, there is some evidence for stress-assisted autocatalysis if it is indeed true that adjacent sheaves form in such a way as to help accommodate each other's shape deformation.

The concept of autocatalytic nucleation may be related to that of sympathetic nucleation, defined by Aaronson and Wells[11] as the nucleation of a precipitate crystal at the interphase boundary of a previously formed crystal of the same phase when the matrix and precipitate differ in composition. Although in discussing sympathetic nucleation, volume strain energy "can be effectively ruled out" according to Aaronson,[44] it seems clear that many examples of this phenomenon would be alternatively interpreted as autocatalytic nucleation by other workers.

2. *Phenomenological theory*

We have seen that the bainite transformation exhibits crystallographic features and surface relief effects similar to those associated with martensitic reactions. It is then natural to assume that the phenomenological theory of martensite crystallography[125,126] should be applicable to bainite. The crystallographic theory predicts a unique relationship between the habit plane, shape deformation, orientation relationship, lattice types, and lattice-invariant deformation. It can only be tested satisfactorily when these variables are not determined in isolation. Much of the early data (reviewed by Bowles and Kennon[127]) are incomplete in this sense but consistent with the theory. All of the early measurements of habit planes must now be interpreted to refer to the habit planes of bainite sheaves, rather than of the individual subunits.

Finally, we note that a considerable difficulty in applying the theory to bainite is the lack of accurate structural information relating to the transformation which is needed as input data. Thus, if bainite grows with a full supersaturation but the carbon escapes in a very short time, the measured lattice parameters of upper bainitic ferrite will not relate to the initially formed structure, which may even have been tetragonal. A similar difficulty exists for lower bainite if appreciable carbide precipitation has taken place before any measurements are possible.

Srinivasan and Wayman[56,57] reported the first detailed results on the crystallography of sheaves of lower bainite in an Fe-1.11C-7.9Cr wt pct alloy ($B_s \sim 300$ °C, $M_s \sim -34$ °C) in which large quantities of austenite remained untransformed at ambient temperature. Each sheaf was found to have just one planar face when examined using light microscopy, and this was taken to be the habit plane. The (irrational) habit plane indices were found to exhibit a small degree of scatter beyond experimental error, the mean indices being close to $(254)_\gamma$ relative to the orientation variant in which $(111)_\gamma$ is almost parallel to $(011)_\alpha$ and $[\bar{1}01]_\gamma$ is at a small angle to $[\bar{1}\bar{1}1]_\alpha$; this is henceforth called the *standard variant*. The martensite habit plane in the same alloy is close to $(494)_\gamma$, and the difference in the two habits and in the exact orientation relations led Srinivasan and Wayman to the conclusion that the mode of displacive transformation is different in bainite and martensite. Their measured habit plane is only about 6 deg from that found for a different alloy by Sandvik, who pointed out, however, that his result applied to an individual platelet whereas that of Srinivasan and Wayman was for the average "habit" of a subpacket or sheath.

The shear component of the shape deformation, as averaged over the entire sheaf, was measured to be ~0.128, the magnitude of the total shape strain being ~0.129. This is consistent with the earlier data of Tsuya[128] and Speich.[65] The actual shape strain for an individual subunit must of course be larger, and was estimated using crystallographic theory as being 0.23; this compares with the 0.28, 0.25, and 0.22 estimated for different alloys by Ohmori,[58] Bhadeshia,[129] and Sandvik,[115] respectively.

Srinivasan and Wayman[56,57] showed that their data on lower bainite are indeed consistent with solutions based on the phenomenological theory of martensite. It was found that the sheaf habit plane and orientation relationship could be predicted for an undistorted habit plane if it is assumed that the lattice-invariant shear is irrational in both plane and direction. On the other hand, if the habit plane is permitted to undergo a small isotropic contraction, then the lattice-invariant shear (for the standard variant) consists of a double shear on the planes $(1\bar{1}1)_\gamma$ and $(101)_\gamma$ in the common direction $[\bar{1}01]_\gamma$ (these correspond to $(101)_\alpha$, $(112)_\alpha$, and $[\bar{1}\bar{1}1]_\alpha$, respectively). This double system is equivalent to a single shear on an irrational plane and is not associated with any of the difficulties encountered in theories which postulate more general combinations of lattice-invariant shears. The component planes on which the interface dislocations would glide are those usually considered as candidates for single lattice-invariant shears in the martensite theory. However, at the time of the Srinivasan and Wayman work, it was not fully appreciated that the so-called habit plane of a sheaf (which they measured) may differ from that of a platelet within a sheaf (which Sandvik measured), and it is not yet clear whether the phenomenological theory of martensite should be applied to the sheaf or the platelet. It may be more important to minimize long-range distortions over the whole sheaf, in which case the invariant-plane condition would apply to the apparent habit plane of the sheaf, but in cases where there are reasonably thick layers of austenite between the platelets, it seems more logical to apply the theory to the individual platelet.

Hoekstra and his co-workers[130,131] recently examined the crystallography of bainite in an Fe-0.35C-0.25Si-0.6Mn-4.5Ni-1.3Cr wt pct alloy isothermally transformed at 365 °C. They used hot-stage light microscopy and a technique for determining the orientation of the austenite using twin vestiges, so that the resulting habit plane data they obtained are assumed to refer to the sheaf habit plane, which was found to be irrational with mean indices $\{569\}_\gamma$. The observed small degree of scatter was attributed to the development of internal stresses during transformation. The ferrite orientation was measured using electron diffraction. The habit plane indices with respect to the ferrite were determined using the criterion that a unique orientation relationship and habit plane should emerge from an analysis of three sets of experimental data. The habit with respect to ferrite was found to be close to $\{2\,7\,10\}_\alpha$, and an analysis of the results led them to conclude that the crystallography of bainite in their samples was inconsistent with the phenomenological theory of martensite. The analysis (Figure 5 of Reference 132) does not, however, seem correct because the angles made by the habit plane pole to the $\{111\}_\gamma \parallel \{011\}_\alpha$ planes and to the $\langle 10\bar{1}\rangle_\gamma \parallel \langle 11\bar{1}\rangle_\alpha$ directions are not in fact the same for the three sets of data analyzed.

3. *The crystallography of a lath of bainite*

It has already been noted that the subunits of a bainite sheaf may adopt the morphology of a plate or of a lath, where the latter is idealized as a parallelepiped of dimensions a, b, and c, with $a > b > c$. There is a general tendency for the lath shape to be adopted when the transformation occurs at relatively high temperatures. The crystallography of such laths has been characterized in detail and to a high level of accuracy by Davenport[60] as follows:

growth direction	$[\bar{1}01]_\gamma \parallel [\bar{1}\bar{1}1]_\alpha$
habit plane (area = *ab*)	$(232)_\gamma \sim \parallel (\bar{1}54)_\alpha$
face of area = *ac*	$(101)_\gamma$
orientation relationship (KS)	$[\bar{1}01]_\gamma \parallel [\bar{1}\bar{1}1]_\alpha$
	$(111)_\gamma \parallel (011)_\alpha$

where the crystallography is for consistency stated in the standard variant described earlier. Hence, the major growth direction of each lath corresponds to the nearly parallel close-packed directions from the α and γ lattices. This is consistent with less direct trace analysis results which indicated that the major growth direction of the laths lies along $\langle\bar{1}\bar{1}1\rangle_\alpha$.[61,63,133] The habit plane indices are significantly different from earlier data which indicated a $\{111\}_\gamma$ habit,[7,61–63] but those analyses were either of insufficient precision or were concerned with the apparent habit planes of sheaves.[60] Davenport also demonstrated that sets of two groups of laths with a common growth direction but with virtually orthogonal habit planes tended to form in close proximity.

There is, as yet, no detailed analysis available which can predict these results.

III. CARBIDE PRECIPITATION

A. *Upper Bainite*

The carbide phase associated with upper bainite is almost always cementite.[21,26,104,134–136]* Upper bainitic ferrite does not itself contain any carbide precipitates.

As a consequence of transformation to bainite, the austenite that is trapped between platelets of upper bainite becomes enriched in carbon. If the carbon concentration of the residual austenite (*i.e.*, x_γ) exceeds that given by the extrapolated $\gamma/(\gamma + \theta)$ phase boundary, then cementite precipitation from the enriched austenite lying adjacent to the platelets of bainitic ferrite becomes thermodynamically possible.[43] This secondary reaction, involving the formation of cementite, reduces the carbon concentration in the residual austenite and is accompanied by the formation of a further amount of ferrite (designated α). The mechanism of this secondary reaction is not fully established, but in view of the very small diffusion coefficients of iron and substitutional atoms at the temperatures involved and the absence of an incoherent interface or grain boundary to start the process, it is unlikely to involve reconstructive transformation. Sandvik[139] has proposed that the decomposition of the residual austenite involves the displacive formation of a triclinic carbide close to cementite in structure and the subsequent formation of a small amount of *bainitic* ferrite. Nakamura and Nagakura,[140] in a study of the second stage of martensite tempering, suggested that cementite and ferrite form directly from austenite, the cementite nucleating on the ferrite/austenite boundaries and growing by rapid diffusion along this boundary, and the secondary ferrite growing martensitically. The sequence of reactions during the process can be summarized as follows:

$$\begin{aligned} \gamma &\rightarrow \gamma + \alpha_{b,\mathrm{SUPERSATURATED}} \\ &\rightarrow \alpha_{b,\mathrm{UNSATURATED}} + \gamma_{\mathrm{ENRICHED}} \\ &\rightarrow \alpha_{b,\mathrm{UNSATURATED}} + \alpha + \theta \end{aligned} \qquad [1]$$

This contrasts with the cooperative growth of cementite and ferrite during the formation of pearlite in plain carbon steels:

$$\gamma \rightarrow \alpha \quad \theta \qquad [2]$$

and with the formation of pearlite in substitutionally alloyed steels:

$$\gamma \rightarrow \alpha + \theta + \gamma' \qquad [3]$$

where γ' is austenite which differs in composition when compared with the original austenite with respect to both substitutional and interstitial solute; the reaction stops when all the phases are homogeneous and of equilibrium composition before all the austenite has transformed.

In planar sections, the cementite particles appear parallel to the traces of habit planes of the bainitic ferrite platelets. Using TEM and extraction replicas, Fisher[141] showed that the cementite particles in upper bainite are in the form of irregular ribbons in three dimensions, particularly when bainite forms at high temperatures. Carbide precipitation also occurs at austenite grain boundaries, and this may influence mechanical properties, especially

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*In steels containing high levels of silicon (~2 wt pct), transition carbides such as κ precipitate first from austenite, but given the opportunity, they tend to transform into cementite.[137] The transition carbide κ has a hexagonal lattice, with a = 6.9 and c = 4.8 Å. Schissler *et al.*[138] reported a new carbide of orthorhombic lattice (a = 6.5, b = 7.7, and c = 10.4 Å), which precipitates from the residual austenite during the bainite reaction in an Fe-1.15C-3.9Si wt pct alloy transformed isothermally at 420 °C. The addition of about 1 wt pct Mn to the alloy changed this to another new carbide, also with an orthorhombic lattice, but with lattice parameters a = 14.8, b = 11.4, and c = 8.5 Å.

toughness.[76] The precipitation of cementite from supersaturated austenite probably first occurs at the austenite grain boundaries so that those carbides can be expected to be relatively coarse.

B. *Lower Bainite*

Lower bainite also consists of a nonlamellar aggregate of ferrite and carbides. However, there are two kinds of carbides. Like upper bainite, precipitation of carbides from the enriched austenite occurs between the bainite platelets. In addition, there is usually a fine dispersion of platelike carbides (ε-carbide or cementite) within the lenticular ferrite plates. As will become apparent, the mechanism of precipitation is different for the two sites.

1. *Precipitation within lower bainitic ferrite*

In contrast to the microstructure obtained after tempering martensite, the carbides found within any given bainitic ferrite plate usually occur in a single crystallographic orientation. When the carbide is cementite, examination of planar sections shows that the particles have their longest axes inclined at some 60 deg to the "growth direction" of the ferrite platelets.[65,142–144] The sharp edges of the ferrite platelets are reported to be free of carbides. The carbides within the bainitic ferrite may or may not touch the sides of the ferrite plates.[129] Of course, the angle quoted must vary as a function of the plane of section; examination has shown that for lower bainitic ferrite that has a habit plane with approximate indices $(0.761\ 0.169\ 0.626)_\gamma$, the cementite precipitates on $(1\bar{1}2)_\alpha$ so that the true angle between the α and cementite habit plane normals is approximately 57 deg.[129] Similar results have been obtained for the angle between the lower bainite sheaf and θ habit plane normals.[58] In some cases, the carbides have been found to form on several different variants of the $\{112\}_\alpha$ planes, although a particular variant tends to dominate.[56,84,145]

Early experiments using Curie point measurements and dilatometry gave indirect indications that the carbide precipitation associated with lower bainite is not always cementite.[36,146,147] Austin and Schwartz[135] first identified the presence of ε-carbide in lower bainite. Since then, several investigators have reported the detection of ε-carbide in association with lower bainite.[63,115,139,145,148–152] Matas and Hehemann[148] interpreted these results by suggesting that the initial carbide in hypoeutectoid steels is ε-carbide, which is then replaced by cementite on holding at the isothermal transformation temperature. The rate at which the ε-carbide converts to cementite increases with temperature, but also depends on steel composition; a high silicon concentration (~2 wt pct) in the steel considerably retards the reaction. This is consistent with the fact that silicon is known to retard the formation of cementite during the tempering of martensite.[153,154,155]

The detection of ε-carbide in lower bainite is important in that it implies the existence of a rather high carbon supersaturation in bainitic ferrite, perhaps to a level of the order of 0.25 wt pct.[156] However, ε-carbide is not always found as a precursor to the precipitation of cementite in lower bainite. Bhadeshia and Edmonds[84] failed to detect ε-carbide in a high-silicon medium-carbon steel (Fe-3.0Mn-2.02Si-0.43C wt pct) even during the early stages of the lower bainite transformation. The steels in which ε-carbide has been observed during the formation of lower bainite are listed in Table I.*

These observations can be rationalized in terms of a theory of tempering due to Kalish and Cohen,[159] who showed that it is energetically favorable for carbon atoms to remain segregated at dislocations when compared with their presence in the ε-carbide lattice.[129] If the dislocation density is high, then sufficient carbon can be tied up at the dislocations so that the ε-carbide stage is missed in the precipitation sequence. In such cases, cementite precipitation occurs directly. Kalish and Cohen estimated that a dislocation density of 2×10^{12} cm^{-2} should prevent ε-carbide precipitation in steels containing up to 0.20 wt pct carbon. Judging from available data (Table I), and if steels containing a large amount of nickel are excluded, then it seems that there is sufficient carbon for the precipitation of a detectable amount of ε-carbide if the average carbon content of the steel is above ~0.55 wt pct. Otherwise, the partitioning of carbon into the residual austenite depletes the bainitic ferrite too rapidly to permit any significant precipitation of ε-carbide. It is believed that nickel enhances the precipitation of ε-carbide,[69] and this is consistent with the lower carbon concentrations (~0.4 wt pct) at which ε-carbide forms during the bainite transformations in these steels. Narashima Rao, and Thomas[160] have demonstrated a similar effect of nickel in martensitic steels; they found ε-carbides and cementite to be the dominant carbides during the tempering of martensite in Fe-0.27C-4Cr-5Ni and Fe-0.24C-2Mn-4Cr wt pct steels, respectively. The other substitutional elements may also have some effect on these phenomena, but this has not been systematically studied. If lower bainite containing ε-carbide is tempered, the latter transforms to cementite and the reaction is accompanied by a volume contraction, which can be monitored accurately using dilatometry.[151]

Finally, η-carbide (Fe_2C) has also been observed in lower bainitic ferrite obtained by transforming the austenite matrix of a high-silicon cast iron.[161,162] This carbide has previously only been reported in tempered martensite[163,164] and so reinforces the conclusion that the carbides precipitate from carbon-supersaturated lower bainitic ferrite. Like ε-carbide, tentative results indicate that the overall carbon concentration of the parent austenite has to exceed some critical concentration before the η-carbide can be readily detected in lower bainite.[161,162]

2. *Precipitation between lower bainitic ferrite platelets*

Since some of the carbon in the alloy is tied up in the form of carbides within the ferrite, the volume fraction of residual austenite trapped between bainite platelets is less for lower bainite.[151] Hence, the decomposition of this austenite into cementite and ferrite leads to a smaller

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*ε-carbide has been reported in bainite produced by continuous cooling transformation in an Fe-0.15C-0.94Mo-2.12Cr wt pct steel[157] and in an Fe-0.34C-1.25Mn-1.39Ni-0.34Mo wt pct alloy isothermally transformed to bainite.[158] In both cases, the evidence quoted is rather indirect.

Table I. Compositions of Steels (Weight Percent) in Which ε-Carbide Has Been Found in Lower Bainite

C	Si	Mn	Ni	Cr	Mo	V	References
0.95							Matas and Hehemann[148]
0.60							Matas and Hehemann[148]
1.00			0.20				Matas and Hehemann[148]
0.58		0.78			0.45	0.90	Matas and Hehemann[148]
1.00		0.36					Deliry[149]
0.60		0.86		0.31			Oblak and Hehemann[63]
0.60							Hehemann[151]
0.41		0.79	1.85	0.75	0.43	0.08	Lai[145]
0.54		0.79		0.30		—	Huang and Thomas[152]
0.74		0.51		0.52			Sandvik[115]
0.40			4.15				Miihkinen and Edmonds[69]

volume fraction of interplate cementite.* The precipitation reactions for lower bainite can be summarized as follows:

Case 1: High dislocation density

$$\begin{aligned} &\gamma \rightarrow \gamma + \alpha_{b,\mathrm{SUPERSATURATED}} \\ &\quad \rightarrow \theta_{\mathrm{IN\ FERRITE}} + \alpha_{b,\mathrm{UNSATURATED}} + \gamma_{\mathrm{ENRICHED}} \\ &\quad \rightarrow \alpha_{b,\mathrm{UNSATURATED}} + \alpha + \theta_{\mathrm{BETWEEN\ FERRITE\ PLATES}} \\ &\qquad + \theta_{\mathrm{IN\ FERRITE}} \end{aligned} \qquad [4]$$

Case 2: Low dislocation density

$$\begin{aligned} &\gamma \rightarrow \gamma + \alpha_{b,\mathrm{SUPERSATURATED}} \\ &\quad \rightarrow \varepsilon\text{-carbide}_{\mathrm{IN\ FERRITE}} + \alpha_{b,\mathrm{UNSATURATED}} \\ &\qquad + \gamma_{\mathrm{ENRICHED}} \\ &\quad \rightarrow \alpha_{b,\mathrm{UNSATURATED}} + \varepsilon\text{-carbide}_{\mathrm{IN\ FERRITE}} + \alpha \\ &\qquad + \theta_{\mathrm{BETWEEN\ FERRITE\ PLATES}} \\ &\quad \rightarrow \alpha_{b,\mathrm{UNSATURATED}} + \theta_{\mathrm{IN\ FERRITE}} \\ &\qquad + \theta_{\mathrm{BETWEEN\ FERRITE\ PLATES}} + \alpha \end{aligned} \qquad [5]$$

A new carbide, which, for convenience, is designated κ-carbide, has been discovered in high-carbon steels transformed to lower bainite.[149,150] It occurs as a transition carbide, precipitating at a late stage of the transformation, from the carbon-enriched residual austenite. Its crystal structure is discussed later (Section III–D). The carbide has a high solubility for Si and, on continued holding at the isothermal transformation temperature, transforms to χ-carbide which, in turn, eventually gives way to the more stable cementite. Similarly, the transition carbide discovered in high-silicon transformer steels by Konoval *et al.*,[165] with an orthorhombic lattice (parameters $a = 8.8$, $b = 9.9$, and $c = 14.4$ Å), has been reported to precipitate from lower bainitic ferrite in Fe-1.15C-3.9Si wt pct alloy.[138]

C. *Kinetics of Carbide Precipitation*

1. *Partitioning and distribution of carbon*

The carbon concentration of bainitic ferrite during transformation is of major importance in determining the kinetics of carbide precipitation; bainite, however, forms at relatively high temperatures and any excess carbon in the ferrite can be removed by the precipitation of carbides within the ferrite or by the diffusion of carbon into the residual austenite. The two mechanisms of carbon removal usually take place simultaneously, although one or the other may dominate, depending on temperature. Both events can be rapid because of the high mobility of carbon in iron.

The partitioning of carbon into austenite lowers its chemical potential. The process was simulated experimentally by Matas and Hehemann,[148] with the help of tempering experiments on mixtures of martensite and retained austenite. Single crystals of austenite (Fe-1.23Cr-0.60Mn-0.13Mo-3.27Ni-0.22Si-0.95C wt pct) were cooled below the M_s temperature (~350 K) to obtain two microstructures, one containing 50 pct martensite and the other 90 pct martensite in a matrix of austenite. The crystals were then tempered at 405 K to allow the carbon to diffuse from martensite into austenite. The tempering treatments caused rapid ε-carbide precipitation in the martensite, precipitation which lowered the carbon concentration of martensite to 0.22 wt pct, a value approximately consistent with that quoted by Roberts *et al.*[156] for the equilibrium between martensite and ε-carbide. Continued holding at the tempering temperature led to further reductions in martensite carbon concentration, the carbon diffusing into the residual austenite. The rejection of excess carbon into austenite occurred more rapidly for the sample containing less martensite because the larger amount of residual austenite provides a bigger sink for carbon.

The distribution of carbon in the residual austenite is not, in general, homogeneous after isothermal transformation to bainite. The austenite is enriched to a greater extent in the immediate vicinity of bainite platelets or in regions trapped between platelets.[148,166] Carbon causes an expansion of the austenite lattice parameter, and, in some cases, two lattice parameters have been observed for the retained austenite, corresponding to different levels of carbon in the austenite within a single specimen.[148] In many cases, the austenite that is relatively

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*A consequence of this is that lower bainite often has a higher toughness than upper bainite, even though it usually is stronger than upper bainite.

poor in carbon decomposes martensitically on cooling to ambient temperature. Any subsequent measurement of the carbon concentration of austenite (x_γ) using an X-ray method would then lead to an overestimation of x_γ if it is assumed that carbon is distributed uniformly in the residual austenite that existed at the isothermal transformation temperature. For example, for upper bainite in a high-silicon steel, X-ray measurements indicated that the carbon concentration of the austenite retained at ambient temperature was about 1.7 wt pct, whereas volume fraction measurements gave an average concentration of 1.35 wt pct for the residual austenite which existed at the transformation temperature.[137]

2. *Kinetics of precipitation from residual austenite*

The incomplete reaction in silicon and some other alloy steels strongly suggests that the precipitation of carbides during the bainite reaction occurs after the formation of bainitic ferrite. Therefore, carbide formation can lag behind that of bainitic ferrite. The extent of this lag depends both on temperature and on alloy composition; for steels which transform rapidly, the lag may not be detectable.

Using a chemical technique which separates precipitated carbon from that in solid solution together with dilatometry, it is possible to show that during the formation of bainite at high temperatures, the amount of carbide formed is proportional to the amount of bainitic ferrite at any stage of the reaction.[167] On the other hand, for lower transformation temperatures, the carbide precipitation reaction is found to lag significantly behind the formation of bainitic ferrite. The steel used to establish these results contained only small concentrations of substitutional solutes and it is likely that an increase in alloy content would, in general, lead to changes in the relative kinetics of all reactions.

With lower bainite, it is necessary to distinguish between the carbides within the bainitic ferrite (which precipitate rather rapidly) and those which form by the decomposition of the carbon-enriched residual austenite which is trapped between the ferrite plates. Transmission electron microscopy studies on an Fe-4.08Cr-0.3C wt pct alloy have shown that of the two reactions which lead to carbide formation in lower bainite, the precipitation of cementite from the residual austenite is a comparatively slow process.[129] Isothermal transformation at 435 °C for 10 minutes (a time long enough to allow the formation of bainitic ferrite to reach completion) gave cementite within the lower bainitic ferrite, but the regions between the ferrite platelets remained as untransformed austenite. It was necessary to hold the alloy at the transformation temperature for a period of 30 minutes before cementite began to precipitate from the residual austenite. The slow rate of this precipitation reaction might indicate that, in contrast to the precipitation within ferrite, it is a reconstructive transformation. However, as suggested by Sandvik,[139] both transformations might be displacive so far as the iron atoms are concerned, and the difference may be ascribable simply to the difference in the diffusion rates of carbon in ferrite and austenite.

The most striking evidence that the formation of carbides from residual austenite lags behind the formation of bainitic ferrite and behind the precipitation of carbides within the ferrite is found in steels containing relatively large amounts of silicon. For example, no carbide formation accompanies the formation of upper bainite in Fe-0.31Cr-0.86Mn-2.00Si-0.60C wt pct alloy, even after holding at the isothermal transformation temperature for several hours.[148] Similar results have been reported by LeHouillier *et al.*[137] and by many other researchers.

Silicon is usually present in steels as an aftermath of the deoxidation reactions involved in the steelmaking process. However, it is clear that the effect of relatively large deliberate additions of silicon on the upper bainite reaction is to retard the formation of cementite from austenite, thereby giving a microstructure of just bainitic ferrite and austenite.[84,137,149–151,168] Silicon in cast irons has long been known to favor the formation of gray cast iron, which contains large amounts of graphite instead of the cementite found in low-silicon white cast irons. The precipitation of cementite during the tempering of martensite is significantly retarded by the presence of silicon,[2,153–155,169,170] and the phenomenon has been used in the design of one of the most successful ultrahigh-strength steels (commercial designation 300M).[171]

The effect of silicon is generally reconciled with the fact that its solubility in cementite is very small. It intuitively seems reasonable that high-silicon steels consequently form a poor environment for the precipitation of cementite. The need for silicon to diffuse away from the cementite/ferrite interface could explain the retardation of its growth.[153] During the tempering of martensite in high-silicon steels, the retardation of cementite growth allows transition carbides to persist for longer periods. At one time, it was thought that the effect is really due to the stabilization of the transition carbides, which have a high solubility for silicon, rather than the retardation of cementite growth,[154,172] but recent work shows that the transition carbides are not particularly enriched with respect to silicon.[173]

Aluminum in solid solution is also believed to retard tempering reactions.[174,175,176] In all respects, aluminum seems to behave in a similar way to silicon with respect to both the bainite and martensite transformations, although detailed data, for example on its solubility in carbides, are not available.

The fact that carbide precipitation from residual austenite lags behind that from bainitic ferrite is also established for steels containing little or no silicon or aluminum. In an Fe-0.3C-4.08Cr wt pct alloy isothermally transformed to lower bainite at 435 °C for 10 minutes, the phase between the cementite-containing ferrite platelets is found to be austenite, whereas if the sample is held at the transformation temperature for 30 minutes, the austenite is replaced with cementite.[129] Heavily alloyed, low-carbon steels also show this effect: in an Fe-0.06C-0.27Si-1.84Mn-2.48Ni-0.2Mo wt pct alloy, no cementite could be detected long after the cessation of the bainite transformation at 460 °C. It was only after a mixture of bainitic ferrite and carbon-enriched austenite (obtained by isothermal transformation at 460 °C) was annealed at 600 °C for 2 hours did cementite formation eventually occur.[177] A similar effect can be found in copper-containing steels, where cementite formation only occurs after annealing the mixture of bainitic ferrite and retained austenite at an elevated temperature.[178]

3. *Kinetics of precipitation within bainitic ferrite*

It is particularly interesting that the precipitation of cementite from martensite or lower bainite can occur under conditions where the diffusion rates of iron and substitutional atoms are very small compared with the rate of precipitation. The long-range diffusion of carbon atoms is of course necessary, but, because of its interstitial character, substantial diffusion of carbon remains possible even at temperatures as low as −60 °C.[179]

Thus, the formation of cementite in these circumstances must differ from the normal reconstructive decomposition reactions, which should become too sluggish at low temperatures. For this reason, it has been believed for some time that the cementite lattice may be generated by the deformation of the ferrite lattice, combined with the necessary diffusion of carbon into the appropriate sites. The ways in which the ferrite lattice could be deformed to produce the right arrangement of iron atoms needed to generate the cementite or ε-carbide structures have been considered phenomenologically by Andrews[180] and Hume-Rothery *et al.*,[181] and the subject has been reviewed by Yakel.[182] The models are not, however, sufficiently developed to predict transformation kinetics apart from suggesting that if the diffusion of iron is not necessary, the precipitation reaction may be relatively rapid.

D. *Crystallography of Carbide Precipitation in Bainite*

Some of the details of the crystal structures of the carbides found in bainite or in tempered bainite are presented in Table II; a comprehensive review has recently been published by Yakel.[182]

During normal isothermal transformation to bainite, *i.e.*, where the steel has not been held at temperature for periods long enough to allow long-range substitutional atom diffusion, only ε-carbide, η-carbide, or cementite precipitate within bainitic ferrite, and only cementite or κ-carbide precipitate from the carbon-enriched austenite between the ferrite platelets. The other carbides form during tempering or during prolonged holding at the isothermal transformation temperature. Shackleton and Kelly[189,190] reported that on rare occasions, $M_{23}C_6$ and M_7C_3 could be found as transformed bainite, but the heat treatment they used was not fully specified, and the observations subsequently have not been verified. The crystal system of M_7C_3 is conventionally reported as hexagonal ($a = 13.982, c = 4.506$ Å), but there is evidence that it is better regarded as an ordered orthorhombic structure.[187]

1. *Cementite: Orientation relationships*

Shackleton and Kelly[189,190] conducted a very detailed and extensive study of the orientation relationships that exist between ferrite and carbides in bainite. The carbides within lower bainitic ferrite were always found to exhibit the orientation relationships observed for cementite that forms during the tempering of supersaturated martensite. As with martensite, the most frequently observed orientation relationship, also called the tempering or Bagaryatski[188] relationship, was found to be

$$\{001\}_\theta \parallel \{211\}_\alpha$$

$$\langle 100\rangle_\theta \parallel \langle 0\bar{1}1\rangle_\alpha$$

The next most frequently observed α/θ orientation relationship, which is also consistent with the tempering of martensite, was found to be

$$\{001\}_\theta \parallel \{\bar{2}\bar{1}5\}_\alpha$$

$$\langle 100\rangle_\theta \text{ within 2.6 deg of } \langle 3\bar{1}1\rangle_\alpha$$

$$\langle 010\rangle_\theta \text{ within 2.6 deg of } \langle 131\rangle_\alpha$$

For the cementite that precipitates during the formation of upper bainite, Shackleton and Kelly showed that the large number of observed orientation relationships could all be rationalized if it is assumed that the cementite precipitates from austenite with the Pitsch[191] γ-θ relationship:

$$\{001\}_\theta \parallel \{\bar{2}25\}_\gamma$$

$$\langle 100\rangle_\theta \text{ within 2.6 deg of } \langle \bar{5}5\bar{4}\rangle_\gamma$$

$$\langle 010\rangle_\theta \text{ within 2.6 deg of } \langle \bar{1}\bar{1}0\rangle_\gamma$$

The α-θ relationships can be generated from the γ-θ relationship by allowing the ferrite to be a variant of the KS α-γ orientation relation.

These results have been confirmed subsequently[86,129] and are important in understanding the mechanism of the bainite transformation; they suggest that in lower bainite, the carbides precipitate from ferrite which is supersaturated with respect to carbon, since the same θ/α orientations are found during the tempering of martensite.

The θ/α orientation relationship found by Isaichev[192] has also been reported for the cementite within lower bainitic ferrite.[58,152] It is in fact quite close to the Bagaryatskii relationship (the two are difficult to distinguish experimentally), and in terms of rational indices, the Isaichev orientation relationship can be written

$$\langle 010\rangle_\theta \parallel \langle 1\bar{1}\bar{1}\rangle_\alpha$$

$$\{103\}_\theta \parallel \{101\}_\alpha$$

2. *The habit plane of cementite*

Using single-surface trace analysis, Shackleton and Kelly showed that for the tempering orientation relationship, the habit plane of cementite in lower bainitic ferrite is in the vicinity of the zone containing $\{1\bar{1}2\}_\alpha$ and $\{0\bar{1}1\}_\alpha$ (corresponding to $\{101\}_\theta$ and $\{100\}_\theta$, respectively). The results are vague because of the irregular shape of the cementite particles and because of the inaccuracies in the technique used. The long dimension of the cementite laths was found to be $\sim\langle 1\bar{1}\bar{1}\rangle_\alpha$ (corresponding to $\langle 010\rangle_\theta$). Note that for these data, the crystallographic indices have justifiably been quoted with respect to both the α and θ lattices, since some of the trace analyses were carried out using diffraction information obtained simultaneously from both lattices. The results are qualitatively consistent with the habit plane of cementite containing the direction of maximum coherency between the ferrite and cementite lattices, *i.e.*, $\langle 010\rangle_\theta \parallel \langle 1\bar{1}\bar{1}\rangle_\alpha$.[180]

For some alloys, the observation of streaks in electron diffraction patterns has been interpreted to indicate that in those cases, the habit plane of the cementite within lower bainitic ferrite is $\sim\{001\}_\theta \parallel \{211\}_\alpha$.[57] However, similar streaking has been observed for a case where the

Table II. Crystal Structures of Carbides in Bainite or in Tempered Bainite

Carbide	Crystal System	Fe, M/C	References
κ	hexagonal $a = 6.9 \quad c = 4.8$		Deliry[149] and Pomey[150]
	hexagonal $a = 2.735 \quad c = 4.339$	2.4 to 3	Jack[183,184] and Hofer *et al.*[185]
χ	monoclinic $a = 11.563 \quad b = 4.573$ $c = 5.058 \quad \beta = 97.44$ deg	2.2 or 2.5	Hägg[186]
η	orthorhombic $a = 4.704 \quad b = 4.318 \quad c = 2.830$	2	Hirotsu and Nagakura[163]
Fe_3C	orthorhombic $a = 4.525 \quad b = 5.087 \quad c = 6.743$	3.0	
M_7C_3	orthorhombic $a = 4.526 \quad b = 7.010 \quad c = 12.142$	7/3	Morniroli *et al.*[187]
$(Fe, Si)C_x$	orthorhombic $a = 8.8 \quad b = 9.0 \quad c = 14.4$		Konoval *et al.*[165]
$(Fe, Si)C_x$	orthorhombic $a = 6.5 \quad b = 7.7 \quad c = 10.4$		Schissler *et al.*[138]
$(Fe, Si, Mn)C_x$	orthorhombic $a = 14.8 \quad b = 11.4 \quad c = 8.5$		Schissler *et al.*[138]
$M_{23}C_6$	cubic F $a = 10.621$	23/6	
M_6C	cubic F $a = 11.082$	6	
	triclinic $a = 6.38 \quad b = 5.05 \quad c = 4.59$ $\alpha = 90.0$ deg $\quad \beta = 70.1$ deg $\quad \gamma = 84.7$ deg		Sandvik[139]

Note: The designation κ is used for the new carbide discovered by Deliry[149] and Pomey.[150] χ has not been reported for bainite but is found during the tempering of martensite so that there is a possibility that it may occur in bainite. The ratio of iron plus other metal atoms to carbon is designated Fe, M/C. The lattice parameters are stated in angstroms. The actual lattice parameters in any particular alloy must also depend on its detailed chemical composition.

cementite habit plane is $\{201\}_\theta$; the streaking may, therefore, be due to faulting on the $\{001\}_\theta$ planes.[58]

For upper bainite, the carbides precipitate from austenite; it is not, therefore, surprising that the particles do not exhibit a consistent set of habit plane indices with respect to ferrite, although those with respect to the cementite lattice are always found to be close to $\{101\}_\theta$ with a long direction close to $\langle 010 \rangle_\theta$.[189,190]

3. *Three-phase crystallography*

Crystallographic information can be interpreted in much more detail if the data are obtained *simultaneously* from austenite, ferrite, and cementite. The first such experiments were reported by Srinivasan and Wayman,[56,57] and subsequent (contradictory) data were given by Bhadeshia.[129] The two sets of data referred to the standard variant of the austenite-ferrite relation defined above, and using *rational approximations* to the measurements, are as follows:

References 56 and 57

$$[111]_\gamma \parallel [011]_\alpha \parallel [100]_\theta$$
$$[\bar{1}01]_\gamma \parallel [\bar{1}\bar{1}1]_\alpha \parallel [010]_\theta$$
$$[1\bar{2}1]_\gamma \parallel [2\bar{1}1]_\alpha \parallel [001]_\theta$$

Reference 129

$$[111]_\gamma \parallel [011]_\alpha$$
$$[0\bar{1}1]_\gamma \parallel [\bar{1}\bar{1}1]_\alpha$$

$$[0\bar{1}1]_\alpha \parallel [100]_\theta$$
$$[1\bar{1}\bar{1}]_\alpha \parallel [010]_\theta$$
$$[211]_\alpha \parallel [001]_\theta$$

For the first set of data,[56,57] the habit plane of the cementite within the lower bainitic ferrite is found to be $(112)_\alpha$, corresponding to $(101)_\gamma$. Srinivasan and Wayman noted that this is one of the planes for the lattice-invariant deformation for lower bainite, as predicted using the phenomenological theory of martensite, and implied that this may somehow explain the presence of just one crystallographic variant of cementite in lower bainite, as compared with the many found when martensite is tempered. When the lattice-invariant deformation is slip, as is the case for bainite, it is incredibly difficult to establish any microstructural evidence in its support. Srinivasan and Wayman interpreted the presence of the carbide on the appropriate planes to lend support to the proposed mode of lattice-invariant deformation in bainite. It was pointed out that the results may not be general, because they found that for an Fe-3.32Cr-0.66C wt pct alloy, the cementite habit plane seemed to be $\{001\}_\theta$, unlike the case for the more heavily alloyed sample.

Unfortunately, the second set of data[129] is not in agreement with the Srinivasan and Wayman hypothesis, and they noted themselves that the cementite habit plane in another Fe-Cr-C alloy containing less chromium and carbon was $(001)_\theta$ rather than $(010)_\theta$. Thus, although the lattice-invariant deformation may be linked to the nucleation of cementite under some circumstances, it does not provide a consistent explanation in others. It also does not explain why multiple variants of carbides are observed in martensites. Further experimental results are highly desirable to ascertain whether the single dominant variant of cementite formed in lower bainite does have different crystallographic relations with the ferrite in different alloys.

Interphase precipitation

An alternative view is that the cementite of lower bainite nucleates and grows at the austenite-ferrite interface, a process which is well established in the high-temperature precipitation of carbides and is described as "interphase precipitation."[193] The carbon that is necessary to sustain the growth of cementite can be absorbed from the adjacent γ, and it is then not necessary for α to be supersaturated. It is argued that during nucleation, the cementite should adopt an orientation which provides good lattice matching with *both* α and γ. If it happens to be the case that there is only one orientation in space which allows good matching with both the adjacent phases, then the theory indicates that only one crystallographic variant of cementite should precipitate for a given variant of ferrite.

It seems intuitively reasonable that a particle at the transformation interface should attempt to lattice match simultaneously with both the adjacent phases. However, the experimental evidence quoted in support of the model (reviewed by Honeycombe[194]) does not seem adequate. For example, during the interphase precipitation of $M_{23}C_6$ in chromium-rich steels, the carbide (which has a face-centered cubic lattice) adopts a cube-cube orientation with the austenite and a KS orientation with the ferrite. However, $M_{23}C_6$ in austenite always precipitates in a cube-cube orientation with austenite, even in the absence of any ferrite. Suppose that the carbide precipitates in austenite and that the austenite then transforms to ferrite; the latter is likely to adopt a rational Kurdjumov-Sachs type orientation with the austenite and, *consequently*, with the $M_{23}C_6$, the final three-phase crystallography having nothing to do with simultaneous lattice matching between all three phases.

During interphase precipitation, the $M_{23}C_6$ could be completely oblivious of the ferrite, even though it may be in contact with the phase, but the good three-phase crystallography would nevertheless follow simply because the $M_{23}C_6$ has a cube-cube orientation with the austenite. To test unambiguously, the theory requires a system where the particles that form at the interphase interface are able to adopt many different variants of an orientation relation with the austenite. It is suggested that interphase precipitation of Mo_2C is an example suitable for further work.

Given a Bagaryatski orientation relationship between lower bainitic ferrite and its internal cementite particles, and a KS orientation relationship between the ferrite and austenite, it can be shown[129] that the three-phase crystallography expected on the basis of the lattice matching arguments is

$$[100]_\theta \parallel [0\bar{1}1]_\alpha \parallel [111]_\gamma$$

$$[010]_\theta \parallel [1\bar{1}\bar{1}]_\alpha \parallel [\bar{1}01]_\gamma$$

The experimental data for lower bainite[129] clearly do not agree with these orientation relations, the cementite "making no effort" to lattice match with the austenite.* This conclusion remains valid even if the α/γ orientation relation turns out to be of the Nishiyama-Wasserman type.

There is another way of verifying this conclusion. Aaronson *et al.*[195] have modeled the growth of cementite which nucleates at the α/γ interface. In this model, the penetration of the cementite into the adjacent ferrite or austenite is determined by the rate at which either of these phases transform into cementite. The growth of the cementite is treated in terms of a one-dimensional diffusion-controlled growth process. With the Zener approximation of a linear concentration gradient in the parent phase, the penetration of cementite in ferrite (G_α) and in austenite (G_γ) are given by

$$G_\alpha \sim 0.5t^{-0.5}D_\alpha^{0.5}(\bar{c}^\alpha - c^{\alpha\theta})/[2(c^{\theta\alpha} - c^{\alpha\theta})\,(c^{\theta\alpha} - \bar{c})]^{0.5} \tag{6}$$

$$G_\gamma \sim 0.5t^{-0.5}D_\gamma^{0.5}(\bar{c}^\gamma - c^{\gamma\theta})/[2(c^{\theta\gamma} - c^{\gamma\theta})\,(c^{\theta\gamma} - \bar{c})]^{0.5} \tag{7}$$

where, for example, D_α is the diffusivity of carbon in ferrite, $\bar{c}$ is the average carbon concentration in the parent phase (α or γ), $c^{\gamma\theta}$ represents the concentration of carbon in the austenite which is in equilibrium with cementite, and t represents the time after the nucleation event. If it is assumed that $c^{\theta\alpha}$ or $c^{\theta\gamma}$ are much greater than $\bar{c}$, $c^{\alpha\theta}$, or $c^{\gamma\theta}$, the ratio of growth rates is given by

$$G_\alpha/G_\gamma = [D_\alpha^{0.5}(\bar{c}^\alpha - c^{\alpha\theta})]/[D_\gamma^{0.5}(\bar{c}^\gamma - c^{\gamma\theta})] \tag{8}$$

Note that the left-hand side of this equation could be replaced by the corresponding ratio of particle dimensions in the two parent phases. Aaronson *et al.*[195] made the further assumption that the carbon concentrations of the austenite and ferrite before the onset of cementite formation are given by $c^{\gamma\alpha}$ and $c^{\alpha\gamma}$, respectively. This in turn implies a number of further assumptions which are not consistent with experimental data: that carbide formation does not begin until the formation of all bainitic ferrite is complete, that there is no supersaturation of

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*Huang and Thomas[152] have expressed the three-phase crystallography of lower bainitic ferrite, the cementite within this ferrite, and austenite as follows:

$$(100)_\theta \parallel (5\bar{4}5)_\gamma,\ 5.77 \text{ deg from } (101)_\alpha$$

$$(010)_\theta \parallel (10\bar{1})_\gamma \parallel (11\bar{1})_\alpha$$

The three-phase relationship is not, however, based on direct experimental evidence. The angle quoted above has been corrected from the original paper.

carbon in the bainitic ferrite, and that the bainite transformation does not obey the incomplete-reaction phenomenon.

On the basis of these assumptions, the cementite in bainite essentially grows by drawing on the richer reservoir of carbon in the austenite and should therefore penetrate to a far greater extent into the austenite than into the ferrite. Contrary to this conclusion, direct observations prove that in the rare cases where a cementite particle in lower bainite happens to be in contact with the transformation interface, the cementite is confined to the ferrite.[129]

Aaronson *et al.*[195] also concluded that since the model predicts that the interphase growth of cementite occurs into both bainitic ferrite and austenite, the debate about whether the carbides nucleate in α or γ is irrelevant. This is not justified because it assumes that the carbides nucleate at the interphase interface, whereas it is likely that the carbides which precipitate within the lower bainitic ferrite nucleate and grow from the supersaturated bainitic ferrite.

4. *Relief of strain energy*

Therefore, the evidence seems to suggest that the occurrence of a single crystallographic variant of carbide in lower bainite cannot be explained in terms of either the interphase precipitation model or the lattice-invariant shear arguments. A possible alternative explanation is that the variant which forms is one that is best suited toward relieving the elastic strains associated with the austenite-to-lower bainite transformation.[129] The observation that carbide precipitation modifies the surface relief of lower bainite[196] supports this conclusion, particularly since freshly formed plates (apparently without carbide precipitation) exhibit perfect invariant-plane strain relief.

5. *Epsilon-carbide*

The orientation relationship between ε-carbide in tempered martensite was deduced by Jack[183,184] as

$$(101)_\alpha \parallel (10\bar{1}1)_\varepsilon$$
$$(2\bar{1}1)_\alpha \parallel (10\bar{1}0)_\varepsilon$$

which also implies that

$$(101)_\alpha \sim 1.37 \text{ deg from } (10\bar{1}1)_\varepsilon$$
$$[100]_\alpha \sim 5 \text{ deg from } [11\bar{2}0]_\varepsilon$$

The first reported crystallographic results for ε-carbide in lower bainite seem to be those of Lai,[145] who observed that $\langle 100\rangle_\alpha \parallel \langle 11\bar{2}0\rangle_\varepsilon$ and, therefore, concluded that the orientation relationship was that found in tempered martensite. However, although his data are consistent with the tempered martensite orientation relationship within the limits of experimental error, they are incomplete since a minimum of two pairs of parallel vectors need to be stated in order to specify the relationship between two crystals. A more detailed study by Huang and Thomas[152] has subsequently confirmed that the ε-carbide found in lower bainite does indeed obey the same orientation relationship with bainitic ferrite as is found during the tempering of martensite.

The ε-carbides are found to occur in the form of plates which are approximately 6 to 20 nm thick and 70 to 400 nm long.[152] The carbide/ferrite interface tends to be ragged, but on a more macroscopic scale, single-surface trace analysis suggests that the carbide particles grow along $\langle 100\rangle_\alpha$ directions on $\{100\}_\alpha$ habit planes.[145]

Huang and Thomas[152] concluded that the ε-carbides precipitate at the austenite/bainitic ferrite interface, on the grounds that the observed orientation between the bainitic ferrite and ε-carbide could be generated by assuming a KS α/γ orientation and a relationship between ε-carbide and austenite in which

$$(111)_\gamma \parallel (0001)_\varepsilon$$
$$(1\bar{1}0)_\gamma \parallel (1\bar{2}10)_\varepsilon$$

Sandvik[115] experimentally verified the Huang and Thomas relations. His ε-carbide formed after 30 minutes at 380 °C but took from 3 hours to 5 days at 320 °C, and he suggests it forms on the interface between bainite and small regions of austenite twins which were left untransformed within the bainite.

6. *Eta-carbide*

Eta-carbide is a transition Fe_2C carbide of the orthorhombic crystal system. It is usually associated with the tempering of martensite,[163,164] where the martensite/carbide orientation relationship is found to be as follows:[163]

$$(110)_\eta \parallel \{010\}_\alpha$$
$$[001]_\eta \parallel \langle 100\rangle_\alpha$$

The carbide has recently been found in lower bainitic ferrite in the austenitic matrix of a high-silicon cast iron,[161,162] where electron diffraction confirms that

$$[001]_\theta \parallel \langle 100\rangle_\alpha \parallel \langle 0\bar{1}1\rangle_\gamma$$

This information is consistent with the η-carbide/martensite orientation relationship stated earlier[163] and lends further support to the hypothesis that the carbides within lower bainitic ferrite precipitate in a manner analogous to the tempering of martensite.

Franetovic *et al.*[161,162] also deduced, by examining the zone axes of their diffraction patterns, that

$$[010]_\theta \parallel \langle 012\rangle_\alpha \parallel \langle \bar{1}11\rangle_\gamma$$

However, the zone axes of the three superimposed patterns could be far from parallel, and this particular set of data is doubtful. Indeed, if the parallelisms are assumed, then the Nishiyama-Wasserman orientation relationship implied between the austenite and ferrite lattices does not follow. More research is needed to establish fully the three-phase crystallography of η-carbide, austenite, and bainitic ferrite.

E. *Chemical Composition of Bainitic Carbides*

It has long been established, using magnetic, chemical, and X-ray methods on extracted carbides, that the cementite associated with upper bainite in alloy steels has a substitutional solute content which is close to, or slightly higher than that of the steel as a whole, even though the cementite composition may be far from the equilibrium composition (*e.g.*, Reference 26). Recent work is in broad agreement with the early data; Chance and Ridley[197] found that for upper bainite in an Fe-0.81C-1.41Cr wt pct alloy, the partition coefficient, k_{Cr}, defined as (wt pct Cr in θ)/(wt pct Cr in α), could not be distinguished from unity (Figure 2). Chance and Ridley suggested that the reason why segregation is found in pearlite but not in bainite (for the same transformation temperature) is that there is a fast diffusion path along the incoherent interface for pearlite.

IV. THERMODYNAMICS AND KINETICS

A. *Equilibrium and Deviations from Equilibrium*

Equilibrium is said to exist in a system when it reaches a state in which no further change is perceptible, no matter how long one waits.[198] A bainitic microstructure is, however, far from equilibrium. As an example, the free energy change accompanying the formation of bainite in an Fe-0.1C wt pct alloy at 540 °C is ~−580 J/mol, whereas that accompanying the formation of an equilibrium mixture of allotriomorphic ferrite and austenite at the same temperature is ~−1050 J/mol. Consequently, the excess energy of bainite could, in this case, be said to be ~470 J/mol, or ~0.04 in units of RT_M, where R is the gas constant and T_M the absolute melting temperature. This is about an order of magnitude larger than the stored energy due to severe cold deformation of pure metals (~0.003 RT_M) but is small in comparison with that of some highly metastable materials such as rapidly quenched liquids which solidify as highly supersaturated solutions ~1 RT_M or multilayered structures with an excess energy of ~0.1 RT_M.[199]

In spite of the large deviations from equilibrium, we shall see that the concepts of equilibrium, metastable equilibrium, and constrained equilibrium can nonetheless be useful in interpreting the mechanism and consequences of the bainite transformation.

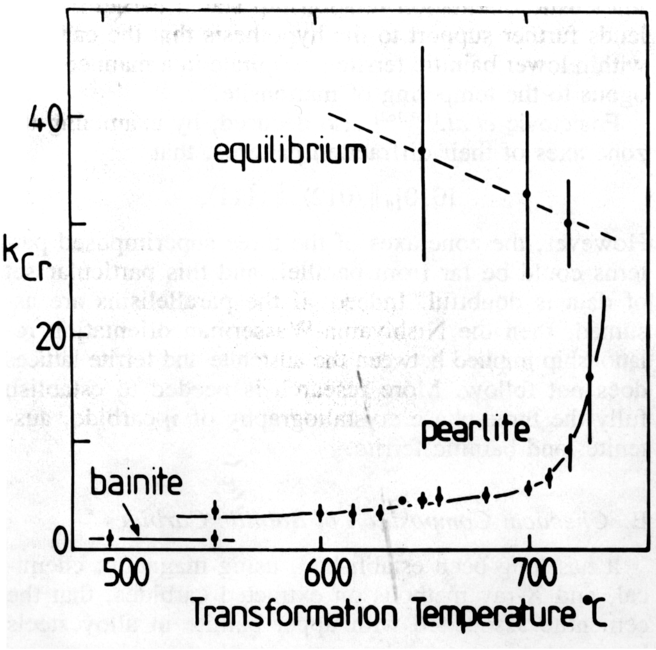

Fig. 2—Partitioning coefficient of chromium between cementite and ferrite, as a function of transformation temperature.[197] For the pearlite, the partitioning coefficients are measured in the pearlite at the pearlite/austenite interface.

Equilibrium is said to exist between homogeneous phases when the chemical potential of each component is the same in all the phases present. It is defined by the equation

$$\mu_i^\gamma = \mu_i^\alpha \qquad [9]$$

for $i = 1, 2, 3 \ldots$, where μ_i is the chemical potential of component "i." In the study of the kinetics of transformations, the concept of equilibrium in terms of phases which are *homogeneous* is rather restrictive. It is then useful to consider equilibrium to exist locally. For example, it is a reasonable approximation that during diffusion-controlled transformation, the compositions of the phases in contact at the interface are such as to allow equilibrium to exist locally even though the phases may not be homogeneous. As long as the phases are not too inhomogeneous (as is the case with some artificial multilayered structures or during spinodal decomposition) classical equilibrium thermodynamics can be applied locally.

As discussed earlier, during paraequilibrium transformation, the ratio of iron to substitutional solute atoms remains the same everywhere, but subject to that constraint, the carbon atoms achieve equality of chemical potential in all phases. Either the substitutional solute atoms or the iron atoms are then said to be trapped by the advancing transformation interface, the criterion for trapping requiring that the chemical potential of that species increases on transfer across the interface.

Transformation may also occur without any diffusion, but this is thermodynamically only possible below the T_o temperature, where the parent and product phases of the same composition have equal free energy.

The concepts of local equilibrium, paraequilibrium, and diffusionless transformation are relatively easy to visualize and formulate and, hence, are very popular. However, between local and paraequilibrium, there could exist an infinite number of states in which the substitutional elements partially partition between the phases. Similarly, between paraequilibrium and diffusionless transformation there can exist an infinite number of states in which the degree of partitioning of carbon may be different from equilibrium. On the other hand, such states would have to be stabilized by some other rate-controlling factor such as interface kinetics; otherwise, they should tend to degenerate toward equilibrium, because any small perturbation in composition at the interface, which leads to a reduction in free energy, would tend to grow. We shall see that the stabilization of such nonequilibrium states is, at least in principle, feasible for solid-state transformations in steels.

Before these concepts can be utilized in assessing the mechanism of the bainite reaction, it is necessary to consider additional terms which raise the free energy of the product phase. For example, the effect of including the stored energy terms is to change the temperature at which composition-invariant transformation becomes thermodynamically possible from T_o to T_o'.

B. *Stored Energy Due to Transformation*

Much of the stored energy of bainite comes from the strain energy due to the invariant-plane strain shape change accompanying transformation. If the shape of a platelet of bainite is approximated as that of an oblate ellipsoid of semi-axes R, R and y, with $R \gg y$, then Christian[200] has shown that the molar strain energy, G_s, which is a consequence of the shape change, is given by

$$G_s = [\mu V_m/(1 - \nu)]\{(2/9)(1 + \nu)\Delta^2 + (\pi y/4R)\xi^2 + ((1 - \nu)\pi y/3R)\Delta\xi\} + 0.5\mu V_m[(2 - \nu)\pi y/4(1 - \nu)R]s^2 \qquad [10]$$

where μ and ν are the shear modulus and Poisson's ratio, respectively, of the matrix austenite, V_m is the molar volume of the austenite, Δ is the uniform dilatation accompanying transformation, ξ is the additional uniaxial dilatation normal to the habit plane, and s is the shear component of the shape change. Although the Δ term has in the past been used to explain the crystallography of bainite, direct measurements of the shape change have not revealed any significant uniform dilatation. Calculations indicate a strain energy term due to the shape change is about 400 J/mol for bainite,[59] this being smaller than the corresponding term for martensite, which is about 600 J/mol.[201] The smaller value for bainite is because the aspect ratio (y/R) for bainite platelets is usually found to be considerably smaller than that for martensite. The shear and dilatational components of the shape change are, in fact, rather similar for martensite and bainite.

There are some complications in using Eq. [10] for the bainite transformation. Bainite platelets do not form in isolation, but grow in sheaves which themselves have a platelike morphology on a macroscopic scale; the shear component of the shape change as averaged over the whole sheaf is much smaller than that of an individual platelet.[56,57,65,128] The effect of such three-dimensional formations of platelets on the stored energy term has not been investigated. Bainite forms at relatively high temperatures where both the austenite and ferrite have low yield strengths. Consequently, the strain energy due to the shape change can be reduced by plastic relaxation. The plastic deformation causes an increase in dislocation density, but since it is driven by the shape change, the strain energy calculated on the basis of an elastically accommodated shape change should be an upper limit.[201] Another complication, which should lead to a reduction in stored energy per unit volume as transformation proceeds, is that new sheaves may grow adjacent to those already existing in a mutually accommodating manner. As the transformation proceeds, carbides grow either from austenite or from the bainitic ferrite; these may grow in such a way as to anneal the transformation strains.

In martensitic reactions, transformation twinning can contribute ~100 J/mol of stored energy;[201] this term does not arise for bainite where the lattice-invariant shear is always found to be slip. Also, the contribution from the bainite/austenite interface is very small during the growth stage.[59]

C. *Thermodynamics of Growth*

Atom-probe experiments, which reveal directly the absence of any substitutional alloying element partitioning at the bainitic ferrite/austenite interface, even on the finest conceivable scale, prove that the growth of bainite in alloy steels cannot be treated in terms of local equilibrium or of any intermediate state between local and paraequilibrium. The atom probe experiments have now been carried out for a wide range of steels, and it is established that Mn, Ni, Si, Cr, and Mo do not redistribute during transformation.[89–93]

It remains to consider the role of carbon in the growth of bainite. This is difficult to resolve directly because if the bainite is supersaturated during growth, the relatively high temperatures at which it grows provide an opportunity for much of the excess carbon to diffuse rapidly into the residual austenite before any experimental measurements can be conducted. The time involved may typically be less than a second;[202] of course, the time does increase as the temperature is reduced but the excess carbon can then precipitate in the form of carbides within the bainitic ferrite. If attempts are made to drastically reduce the transformation temperature by alloying, then bainite ceases to form, leaving martensite as the only displacive transformation product of austenite.[203]

However, there are indirect methods of determining the carbon concentration of bainitic ferrite during growth. If bainitic ferrite initially has the same composition as the parent austenite, the transformation should in principle go to completion since there is no diffusion necessary. In practice, the whole of the austenite grain does not transform instantaneously because of kinetic restrictions (*e.g.*, heterogeneous nucleation and the fact that the plates reach a limiting size); even if the first plate of bainite forms without any diffusion, it has an opportunity to reject its excess carbon into the remaining austenite during the progress of the reaction as a whole. This is a reflection of the fact that at the temperatures where bainite typically forms, the time required for partitioning is not large when compared with that for the reaction to terminate. Because the austenite becomes enriched with carbon, a stage is eventually reached when it is thermodynamically impossible for further bainite to form by diffusionless transformation. At this point, the composition of the austenite is given by the T_o' curve of the phase diagram. If the alternative hypothesis is that paraequilibrium exists during all stages of transformation, then the reaction would stop when the carbon concentration of the austenite is given by the $Ae3''$ curve. The $Ae3'$ curve is the $(\alpha + \gamma)/\gamma$ paraequilibrium phase boundary, and the $Ae3''$ curve is obtained when this is modified to account for the stored energy of transformation. The reaction is experimentally found to stop when the average carbon concentration of the austenite is close to the T_o' curve rather than the $Ae3''$ boundary. The experimental evidence has been reviewed by Christian and Edmonds[24] and is based on dilatometry, lattice imaging, and atom-probe techniques.

Therefore, the reaction remains incomplete in the sense that there is no equilibrium between the austenite and ferrite and that the volume fraction of bainitic ferrite does not satisfy the lever rule. Note that the difference in carbon concentrations between the T_o' and $Ae3''$ curves at the temperatures where bainite typically forms is very large, so that the experiments mentioned above are a sensitive indication of the failure of the transformation to reach paraequilibrium. This "incomplete-reaction phenomenon" explains immediately why the degree of transformation to bainite is zero at the B_s temperature and increases with undercooling below B_s in steels where other reactions do not overlap with the formation of bainitic ferrite; the T_o' curve has a negative slope on a temperature/carbon concentration plot, so that the austenite can tolerate more carbon before diffusionless transformation becomes possible as the temperature is reduced.

The incomplete-reaction phenomenon supports the hypothesis that the growth of bainitic ferrite occurs without any diffusion, with carbon being subsequently partitioned into the residual austenite. There is as yet no reasonable alternative explanation of this phenomenon.

Consider now the possibility that the ferrite during growth is only partially supersaturated with carbon. The driving force available for transformation can be partitioned into that dissipated in the diffusion of carbon ahead of the interface and a quantity dissipated in the transfer of atoms across the interface. Each of these dissipation terms can, with an appropriate model, be related to interface velocity functions, one being the diffusion velocity and the other a velocity determined by the mobility of the interface. The intersection of these functions gives an actual solution of the interfacial velocity. By imposing different levels of supersaturation in the ferrite, a series of solutions can be calculated as a function of supersaturation. Some criterion (*e.g.*, maximum velocity) can then be used to select the most likely solution and, hence, the most likely supersaturation. In this way, it has been shown,[204,205] using what seems to be a realistic model of the interface, that growth involving partial supersaturation can be stable, as pointed out by Christian and Edmonds. Using different physical principles, the same conclusion has also been reached by Hillert.[206]

Nonetheless, there remain numerous difficulties with the concept of growth with partial supersaturation in the context of bainite in steels. The models all predict that the degree of supersaturation rises with undercooling; this is inconsistent with the fact that the bainite reaction stops when the carbon concentration of the residual austenite approaches the T_o curve. At first sight, the consequence of increasing supersaturation with undercooling would be to change the terminal carbon concentration of the austenite from the $Ae3''$ down to T_o' at full supersaturation as the transformation temperature is reduced. On the other hand, for a given transformation temperature, one might expect the level of supersaturation to decrease as the transformation progresses (since the austenite becomes enriched in carbon), so that the terminal carbon concentration may then always be given by the $Ae3''$, irrespective of transformation temperature.

A further difficulty is that at a given transformation temperature, it is predicted that for growth involving partial supersaturation, the terminal carbon concentration of the austenite cannot be less than a value x_m^γ, where x_m^γ is determined by the tangent to the austenite free energy curve, the tangent being chosen such that it intersects the ferrite free energy curve at the average alloy carbon concentration, $\bar{x}$. This is again inconsistent with experimental measurements.[89,90]

It is pertinent to note that the models for growth involving partial supersaturation are not as yet fully developed. They do not, for example, take account of stored energy or plate aspect ratio variations as a function of temperature, nor do they predict the stifling of the growth of individual platelets of bainite.

If partial supersaturation is not possible, then some explanation is needed as to why there is an abrupt transition from paraequilibrium growth for Widmanstätten ferrite and diffusionless growth for bainite. We propose that an abrupt transition may be expected if, in addition to the requirement that diffusionless transformation is only permitted below T_o', it is also necessary to consider the relative kinetics of interface motion and of the partitioning of carbon from the supersaturated ferrite behind the advancing interface into the residual austenite. If the kinetics of the latter process are comparable to the rate at which the interface advances, then the diffusion fields of the two phenomenologically different processes must overlap, and growth should tend to reduce toward equilibrium partitioning. This is a distinct possibility at high temperatures (still below T_o') because the decarburization of ferrite is then very rapid.[202] It is necessary to construct a model of plate growth which accounts for diffusion processes which begin immediately behind the transformation interface to consider this problem in detail. It provides, for the moment, a possible explanation for a relatively abrupt transition from paraequilibrium growth of Widmanstätten ferrite to the diffusionless growth of bainite.

D. *Thermodynamics of Nucleation*

It is an experimental fact that the rate at which the W_s or B_s temperature decreases as a function of alloy chemistry is larger than the corresponding change in the $Ae3$ temperature. This problem has been investigated by Bhadeshia[203] using data from TTT diagrams. Although there is much fine detail in such diagrams, they essentially consist of two *C* curves. The one at lower temperatures has a flat top and represents the formation of Widmanstätten ferrite and bainite.* By analyzing the driving force available at the highest temperature, T_h, where bainite or Widmanstätten ferrite form at a detectable rate as a function of alloy chemistry, it can be deduced that both of these transformation products nucleate by the same mechanism and that the formation of the nucleus involves the equilibrium partitioning of carbon. Interestingly, the driving force necessary to obtain a detectable rate of nucleation was found to decrease linearly as a function of T_h. This behavior is consistent with the theory for martensite nucleation, in which the activation energy is proportional to driving force,[203] whereas classical nucleation theory predicts an inverse square

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*In steels where the transformation kinetics are very rapid, the curves overlap to such an extent that the TTT diagram appears to contain just one *C* curve.

relationship. The implication is that the nucleation process for bainite and Widmanstätten ferrite is like martensite, displacive in character, but, unlike martensitic nucleation which is diffusionless, there is equilibrium partitioning of carbon during the formation of the nucleus. Furthermore, the theory predicts, as observed experimentally, that a larger driving force is needed to achieve a given nucleation rate if the transformation temperature is depressed by alloying. This clearly is consistent with the fact that the effect of alloying in depressing the B_s and W_s temperatures is greater than on the $Ae3$ temperature.

If at T_h the available driving force is insufficient to sustain the diffusionless growth of bainite, then $T_h = W_s$. A further undercooling is then necessary before the B_s temperature is reached. On the other hand, if sufficient driving force is available at T_h to account for both diffusionless transformation and the stored energy of bainite, then Widmanstätten ferrite does not form in the steel concerned. Similarly, very heavy alloying can make both the Widmanstätten ferrite and bainite reactions to be absent, since the temperature is then sufficiently low to permit directly the diffusionless nucleation and growth of the kinetically favored martensite. These concepts explain why all three transformations do not necessarily occur in all steels.

E. *Growth Rate*

1. *Growth rate of sheaves of bainite*

Sheaves of bainite normally nucleate at austenite grain boundaries and propagate toward the grain interiors by the nucleation and growth of individual subunits. New subunits nucleate near the tips of previous subunits; the nucleation of subunits in adjacent positions occurs at a much lower rate. This means that the sheaf itself has on a macroscopic scale a platelike morphology in three dimensions. Since coordinated movements of atoms cannot in general be sustained across austenite grain boundaries, the growth of a given sheaf is confined strictly to a single austenite grain. Bainite plates are also stopped by austenite twin boundaries.[40,65] The grain in which bainite grows is the one with which it has an orientation within the Bain region as previously defined; this contrasts with the Smith[3] theory of grain-boundary nucleation for reconstructive transformations, which states that the new phase will grow into the grain with which it has a random (incoherent boundary) orientation.

Most direct observations of bainite growth are of limited resolution and refer to the growth of *sheaves* of bainite. Typical thicknesses of "plates" of bainite observed in such studies (*e.g.*, Reference 65) are in the range of 1 to 5 μm, far greater than that of a subunit, as observed using TEM, which is ~0.2 μm. In the discussion that follows, observations using light microscopy are interpreted as referring to sheaf growth, even though the original papers may not make any explicit distinction between sheaf and subunit.

Several direct observations have shown that the lengthening of bainite sheaves occurs at a constant rate.[67,207,208] For a given transformation temperature, the measured rates are found to exhibit a significant degree of scatter, attributed to small variations in growth rate in radial directions within the habit plane of a given sheaf, giving rise to a noncircular habit plane. An increase in carbon, nickel, or chromium concentration leads to a decrease in the lengthening rate. From measurements of the thickening rates of sheaves, Speich and Cohen[207] concluded that the aspect ratio (thickness/length) was independent of sheaf size, the thickening rate being proportional to the lengthening rate, and similar results have been reported by Hawkins and Barford.[67] This does not imply that the thickening and lengthening processes for sheaves are coupled, because thickening was found to continue at the same rate, even when lengthening stopped.*

The ratio of the thickening to lengthening rate (when these are independent of time) determines the aspect ratio of a sheaf whose growth has not been limited by impingement with obstacles such as grain boundaries. The activation energy, Q, of a growth process may be defined as[209]

$$Q = -\mathrm{R}[d(\ln\{G\})/d(1/T)] \qquad 11]$$

This phenomenological relation makes no specific assumptions about the temperature dependence of growth rate, so that the activation energy, Q, cannot be physically interpreted without further justification. The activation energy for lengthening is found to be smaller than that for thickening, so that the aspect ratio of a sheaf is expected to decrease with temperature, as confirmed experimentally. There is, however, no satisfactory theoretical treatment of the kinetics of sheaf thickening, and it is also not established that the rate of thickening is constant, as claimed by Speich and Cohen[207] and Speich.[65] Goodenow and Hehemann[210] found that the thickening rate decreases with increasing thickness.

A recent critical assessment of the data for the lengthening of plates of Widmanstätten ferrite and sheaves of bainite in plain carbon steels demonstrates that for bainite, the measured sheaf growth rates are much higher than would be indicated by carbon diffusion-controlled growth.[211]

2. *Growth rate of individual subunits of bainite*

The lengthening rate of individual subunits of bainite is undoubtedly far less than the speed of sound in the metal (martensite growth velocity is often limited by this). While the shape change accompanying transformation indicates that the bainite/austenite interface is glissile, the rate at which the interface moves is relatively slow, especially if it is accepted that the growth is diffusionless. Goodenow and Hehemann[210] suggested that the slow growth of bainite is associated with the damping of interface dislocation motion at the high temperatures at which bainite forms. There may also be a dissipation of energy

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*These[67,207] and other observations have originally been interpreted to refer to the growth of individual bainite plates rather than sheaves. Speich considered that the thickening process involves the planar motion of the broad face of the plate at a rate controlled by the diffusion of carbon in the austenite, and the observed *constant* thickening rate was then explained by the periodic precipitation of carbides such that the effective diffusion distance for carbon remained approximately constant. The observations really refer to sheaf growth, the rate of thickening depending perhaps on the nucleation of other adjacent subunits.

associated with the movement of carbon atoms in compliance with the interface stress field.

The growth rate of individual subunits of bainite has been measured for an Fe-Mn-Si-C alloy using hot-stage photoemission electron microscopy, and it is found that the subunits lengthen at rates which are orders of magnitude faster than would be expected from carbon diffusion-controlled growth.[212]

3. *Partitioning of carbon from supersaturated bainitic ferrite*

If bainitic ferrite grows with a nonequilibrium concentration of carbon, then, given the opportunity, the carbon should tend to partition into the residual austenite where it has a lower chemical potential.*

The time, t_d, required to decarburize the supersaturated ferrite is intuitively expected at least to be comparable to that required for a subunit to complete its growth. If t_d is small compared with the kinetics of carbide precipitation from ferrite, then the transformation would be classified as upper rather than lower bainite.

Kinsman and Aaronson[213] considered the kinetics of the partitioning of carbon from bainitic ferrite of the same composition as the parent phase. For a plate thickness w, it is reasonably assumed that the flux of carbon is one-dimensional along a coordinate z normal to the α/γ interface, with origin at the interface and z being positive in the austenite. A more recent version of the calculation[202] begins with the conservation condition:

$$(0.5w)\,(\bar{x} - x^{\alpha\gamma}) = \int_{z=0}^{\infty} [x_\gamma\{z, t_d\} - \bar{x}]\, dz \qquad [12]$$

where t_d is the time taken for the ferrite composition to become uniform at its paraequilibrium value, $\bar{x}$ is the average mole fraction of carbon in the alloy, and $x^{\alpha\gamma}$ and $x^{\gamma\alpha}$ are the paraequilibrium carbon concentrations in α and γ, respectively.* Since the diffusion rate of carbon in austenite is slower than in ferrite, the rate of decarburization will be determined by the diffusivity in the austenite, and the concentration of carbon in austenite at the interface remains constant for times $0 < t < t_d$, after which it steadily decreases as the austenite becomes homogeneous in composition. The function x_γ is given by

$$x_\gamma = \bar{x} + (x^{\gamma\alpha} - \bar{x})\ \mathrm{erfc}\ \{z/2(Dt_d)^{0.5}\} \qquad [13]$$

Kinsman and Aaronson evaluated the concentration-dependent diffusivity, $D\{x\}$, of carbon in austenite at $x = x^{\gamma\alpha}$, but it should be a better approximation to take it to be a weighted average diffusivity, $\bar{D}$. On integrating Eq. [13], we get

$$t_d^{0.5} = w(\bar{x} - x^{\alpha\gamma})\pi^{0.5}/4\bar{D}^{0.5}(x^{\gamma\alpha} - \bar{x}) \qquad [14]$$

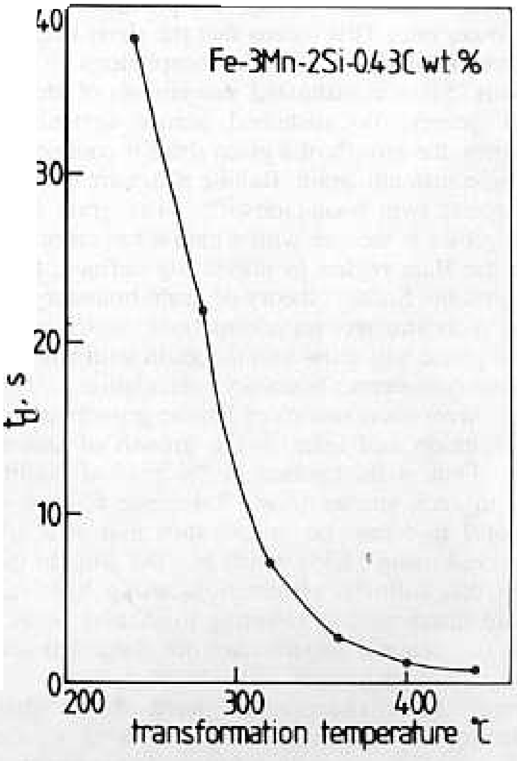
Note also that by substituting different levels of starting carbon concentrations in the ferrite, the time dependence of the average ferrite concentration can also be determined. Kinsman and Aaronson's original estimate was t_d = 3 ms at 540 °C for platelets with a delay time between successive nucleation events of about 10 seconds. The variation of t_d with temperature is shown in Figure 3.

V. REVERSE TRANSFORMATION FROM BAINITE TO AUSTENITE

There has been little work reported on the mechanism or kinetics of the reverse transformation of bainite into austenite, probably because for wrought steels, there is no industrial demand for a knowledge of this process. As a consequence of research on the modeling of microstructures in multirun weld deposits, where the successive deposition of hot layers of weld metal causes some of the underlying metal to reaustenitize, there is now considerable interest in a quantitative description of the kinetics of reaustenitization from bainite.

Reaustenitization from Austenite and Upper Bainitic Ferrite

When an iron-carbon alloy is heated to a temperature within the $\alpha + \gamma$ phase field until equilibrium is established between allotriomorphic ferrite and austenite, a small rise or fall in temperature leads to the growth or dissolution, respectively, of the austenite until the volume fractions once again satisfy the lever rule.[214] The transformation of austenite into allotriomorphic ferrite



ig. 3—Diagram illustrating how the time required to decarburize a late of bainite in an Fe-0.43C-3Mn-2Si wt pct alloy varies with emperature.

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*The tendency for excess carbon to redistribute into the residual austenite should also exist for martensitic transformations in steels. However, these transformations occur at a relatively low temperature, where the time taken to redistribute the carbon is large compared with the time taken to transform most of the austenite. Consequently, the redistribution process does not hinder the progress of martensitic transformation.

*These equilibrium concentrations should strictly allow for the stored energy of bainitic ferrite.

is, in this sense, reversible, and exhibits little or no hysteresis. On the other hand, for martensite in steels, there is a large difference between the M_s and the austenite-start temperature (A_s) recorded during heating. This is because the martensite tempers (or autotempers) and because its formation does some work in the form of irreversible plastic deformation.

If carbides precipitate from the austenite during the bainite reaction, then a considerable hysteresis is expected during reverse transformation which would require the renucleation of austenite. On the other hand, a large hysteresis effect is not expected if reverse transformation begins from an *equilibrium* mixture of just bainitic ferrite and austenite. Of course, if the bainite forms by diffusionless transformation and the excess carbon is rejected into the residual austenite subsequent to transformation, then the reaction would cease before an equilibrium mixture of ferrite and austenite is reached, so that an increase in temperature would not lead to an immediate reversal of transformation.

The problem can be studied best in steels which transform to bainite without any precipitation of carbides. In these circumstances, the microstructure obtained by isothermal transformation below B_s is a mixture of bainitic ferrite and carbon-enriched residual austenite. To study the reverse transformation, the mixture can be heated to an isothermal reaustenitization temperature, so that the nucleation of austenite is unnecessary. Experiments like these have shown that the reaustenitization occurs by a diffusional process and have established clearly that there is indeed a large difference between the B_s and A_s temperatures. This is in spite of the fact that the starting microstructure exists in a metastable $\alpha + \gamma$ phase field. Furthermore, the A_s temperature is found to correspond approximately to the $Ae3$ temperature of the *residual austenite*. The degree of reaustenitization increases from zero at the A_s temperature to 100 pct at the austenite-finish, or A_f, temperature, which is the $Ae3$ temperature of the alloy as a whole. If bainite was simply the product of equilibrium or paraequilibrium transformation, then, like allotriomorphic ferrite, a rise in temperature above the isothermal transformation temperature should lead to a reversal of reaction with little hysteresis.

The observed reaustenitization behavior can be understood as follows.[177,215] In steels where carbide precipitation from austenite is relatively sluggish, the formation of bainite ceases prematurely during isothermal transformation at a temperature T_o'. The stage at which reaction stops is when the carbon content of the residual austenite reaches the T_o' curve of the phase diagram (Figure 4). It follows that the carbon concentration, x_γ', of the austenite when the formation of acicular ferrite ceases at T_i is given by

$$x_\gamma' = x_{T_o'}\{T_i\} \qquad [15]$$

as indicated by the point "a" in Figure 4. Furthermore, we note that

$$x_\gamma' \ll x_{Ae3}\{T_i\} \qquad [16]$$

where $x_{Ae3}\{T_i\}$ is marked "b" in Figure 4.

Thus, although the formation of *bainite* ceases at T_i, because the carbon content of austenite is far less than the equilibrium concentration (*i.e.*, $x_\gamma' \ll x_{Ae3}\{T_i\}$), the net free energy change for further formation of ferrite by a mechanism which includes carbon diffusion is still negative.

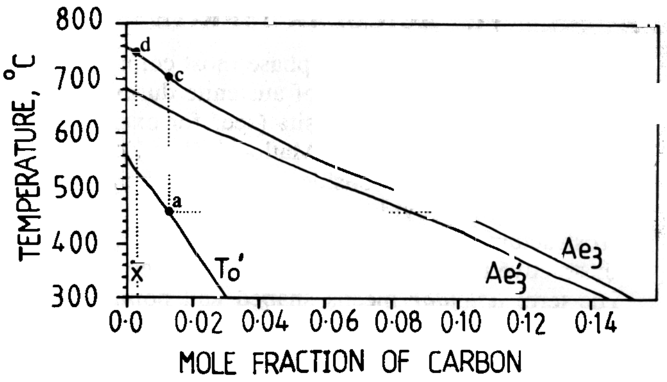

Fig. 4—Phase diagram showing the $Ae3$, $Ae3'$, and T_o' curves for an Fe-0.27Si-1.84Mn-2.48Ni-0.20Mo wt pct alloy.

This remains the case until the temperature, T, is high enough (*i.e.*, $T = A_s$) to satisfy the equation

$$x_\gamma' = x_{Ae3}\{A_s\} \qquad [17]$$

Hence, reaustenitization will first occur at a temperature A_s, as indicated by the point "c" in Figure 4, and as observed experimentally. This is a consequence of the mechanism of the bainite reaction, which does not allow the transformation to reach completion. If this were not the case, then the lever rule demands that the temperature need only be raised infinitesimally above T_i in order for the reverse $\alpha \rightarrow \gamma$ transformation to be thermodynamically possible.

The theory predicts that at any temperature T_γ greater than A_s, the $\alpha_b \rightarrow \gamma$ transformation should cease as soon as the residual austenite carbon concentration (initially x_γ') reaches the $Ae3$ curve, *i.e.*, when

$$x_\gamma = x_{Ae3}\{T_\gamma\} \qquad [18]$$

The equilibrium volume fraction of austenite at the temperature T_γ is then given by

$$V_\gamma\{T_\gamma\} = \bar{x}/x_{Ae3}\{T_\gamma\} \qquad [19]$$

assuming that the carbon concentration of ferrite is negligible and that $x_{Ae3}\{T_\gamma\} > \bar{x}$. When $x_{Ae3}\{T_\gamma\} = \bar{x}$, the alloy eventually becomes fully austenitic (point "d" in Figure 4), and if this condition is satisfied at $T_\gamma = A_f$, then, for all $T_\gamma > A_f$, the alloy transforms completely to austenite.

This model explains why the degree of $\alpha_b \rightarrow \gamma$ transformation increases from approximately zero at A_s (the $Ae3$ temperature of the *residual austenite*) to 100 pct at A_f (the $Ae3$ temperature of the alloy as a whole). The behavior is a direct reflection of the fact that the composition of the residual austenite after the bainite reaction has ceased is far below equilibrium. This in turn provides further support for the incomplete reaction phenomenon and its implication that the growth of bainite occurs without any diffusion. Finally, it should be noted that the model discussed above assumes that the carbon concentrations of both phases are uniform at all stages.

VI. ACICULAR FERRITE

"Acicular ferrite" (α_a) is a phase most commonly observed in the transformation of austenite during cooling of low-alloy steel weld deposits (see, for example, the recent reviews by Grong and Matlock[216] and Abson and Pargeter.[217]) It is of considerable commercial importance because it provides a relatively tough and strong microstructure. It forms in a temperature range where reconstructive transformations become relatively sluggish.

The term *acicular* means shaped and pointed like a needle, but it is generally recognized that α_a has in three dimensions the morphology of thin, lenticular plates (Figure 5). The true aspect ratio of such plates has never been measured, but in random planar sections, the plates are typically about 10 μm long and ~1 μm wide, so that the true aspect ratio is likely to be much smaller than 0.1.

In fusion welding processes involving steels, the use of strong deoxidizing elements such as silicon, aluminum, and titanium, together with protective slag-forming compounds, causes the entrapment of complex multiphase nonmetallic inclusions in the solid at the advancing δ-ferrite/liquid interface. The inclusions may be oxides or other compounds but they can, under some circumstances, influence the subsequent development of microstructure during cooling of the weld deposit. Acicular ferrite plates, during the early stages of transformation, nucleate on inclusions present in the large columnar austenite grains which are typical of weld deposits.[218] Subsequent plates may nucleate autocatalytically, so that a one-to-one correspondence between the number of active inclusions and the number of α_a plates is not expected.[219]

The shape change accompanying the formation of α_a has been characterized qualitatively as an invariant-plane strain; other measurements imply that the stored energy of acicular ferrite is ~400 J/mol.[177,220,221] Consistent with the observed surface relief effect, microanalysis experiments indicate that there is no bulk partitioning of substitutional alloying elements during the formation of acicular ferrite.[220,221] However, work of a higher spatial and chemical resolution is needed to verify the absence of local effects near the transformation interface.

Fig. 5 — A transmission electron micrograph illustrating the morphology of acicular ferrite in a steel weld deposit.

Plates of α_a have never been found to cross austenite grain boundaries, and the orientation relationship between α_a and the γ grain in which it grows is always in the Bain region.[220]

The acicular ferrite transformation obeys the incomplete-reaction phenomenon, the degree of reaction tending to zero as the transformation temperature rises toward the B_s temperature; at a given temperature, the transformation stops as x_γ reaches the T_0' curve. The evidence all indicates that the growth of acicular ferrite is diffusionless, with carbon partitioning into austenite after the transformation event.

The experimental data to date indicate that acicular ferrite is essentially identical to bainite. Its detailed morphology differs from that of conventional bainite because the former nucleates intragranularly at inclusions within large γ grains, whereas in wrought steels which are relatively free of nonmetallic inclusions, bainite nucleates initially at γ/γ grain surfaces and continues growth by the repeated formation of subunits to generate the classical sheaf morphology. Acicular ferrite does not normally grow in sheaves because the development of sheaves is stifled by hard impingement between plates nucleated independently at adjacent sites. Indeed, conventional bainite or acicular ferrite can be obtained under identical isothermal transformation conditions in the same (inclusion-rich) steel; in the former case, the austenite grain size has to be small in order that nucleation from grain surfaces dominates and subsequent growth then swamps the interiors of the γ grains. For a larger γ grain size, intragranular nucleation on inclusions dominates, so that α_a is obtained. Hence, the reason why α_a is not usually obtained in wrought steels is because they are relatively free of inclusions and because most commercial heat treatments aim at a small austenite grain size.

Acicular ferrite is sometimes considered to be intragranularly nucleated Widmanstätten ferrite[219] on the basis of the observation of "steps" at the transformation interface, which are taken to imply a ledge growth mechanism. This kind of evidence is, however, tenuous in the sense that a step mechanism is a mechanism for interface motion and carries no implication about the mechanism of transformation. Furthermore, the observations themselves are weak in the sense that perturbations of various kinds can always be seen on transformation interfaces between ferrite and austenite. Such perturbations do not, however, necessarily imply a step mechanism of growth. Evidence that the residual austenite is enriched in carbon is also quoted in support of the contention that α_a is Widmanstätten ferrite,[219] but, as pointed out above, the enrichment can occur during or after the transformation event.

Referring again to the nucleation of acicular ferrite, it is established theoretically[219] that inclusions are less effective in nucleating ferrite when compared with austenite grain surfaces, and experiments confirm this since ferrite formation first begins at the austenite grain boundaries. However, because of the complexity of the inclusions and the difficulty in conducting controlled experiments with welds, the nucleation potency of inclusions is not clearly understood. A popular idea is that those inclusions which show the best "lattice matching" with ferrite are most effective in nucleating the ferrite, and it has even been suggested[222] that there may exist reproducible orientation relationships between inclusions and the ferrite plates that they nucleate. Experiments, however, demonstrate the absence of a reproducible ferrite/inclusion orientation relationship.[223] The fact that the inclusions, which form in the liquid steel, are randomly oriented in space, and that the orientation relationship of acicular ferrite with the parent austenite is always found to be of the KS/NW type, necessarily implies that the inclusion/ferrite orientation relation also has to be random. Other ways in which inclusions may assist the formation of acicular ferrite include stimulation by thermal strains and chemical heterogeneities in the vicinity of the inclusion/matrix interface; also, the inclusions may simply act as inert sites for heterogeneous nucleation.[224] Chemical reactions are also possible at the inclusion/matrix interface.[225]

VII. CONCLUSIONS

A. *Key Characteristics of Transformations in Steels*

The table below[202] indicates the key characteristics of phase transformations in steels; it may be regarded as a working hypothesis which seems most consistent with the available experimental data. The nomenclature used for the transformation products is as follows: martensite (α'), lower bainite (α_{lb}), upper bainite (α_{ub}), acicular ferrite (α_a), Widmanstätten ferrite (α_w), allotriomorphic ferrite (α), idiomorphic ferrite (α_i), pearlite (P), and substitutional alloying elements (X). Consistency of a comment with the transformation concerned is indicated by ($=$) and inconsistency by ($\neq$); cases where the comment is only sometimes consistent with the transformation are indicated by ($\otimes$). The term *parent* γ implies the γ grain in which the product phase grows. Note that it is not justified to distinguish massive ferrite from α.

B. *Notes*

Nucleation and growth reactions are of first order in the Ehrenfest classification; in all such reactions, the parent and product phases can coexist and are separated by well-defined interfaces. Martensitic transformations, because they can be very rapid in steels, are sometimes incorrectly stated not to involve a nucleation and growth process.

It is significant that all of the ferrite crystals which grow in the form of plates have an invariant-plane shape change with an appreciable shear component accompanying transformation. Pearlitic ferrite does not have a plate morphology, since, within an apparently lamellar colony, the ferrite regions are all interconnected in space.

Reconstructive diffusion is the flow of matter necessary during reconstructive transformation in order to ensure the absence of the sort of shape deformations which accompany the formation of martensite. A reconstructive transformation may be regarded as a combination of a lattice change and a recrystallization of the product phase, reconstructive diffusion being the flow necessary for the recrystallization process.

In diffusionless transformations, it is possible to specify (in a localized region at least) how particular vectors, planes, and unit cells of one structure (defined by an

Comment	α'	α_{lb}	α_{ub}	α_a	α_w	α	α_i	P
Nucleation and growth reaction	$=$	$=$	$=$	$=$	$=$	$=$	$=$	$=$
Plate morphology	$=$	$=$	$=$	$=$	$=$	$\neq$	$\neq$	$\neq$
IPS shape change with shear component	$=$	$=$	$=$	$=$	$=$	$\neq$	$\neq$	$\neq$
Diffusionless nucleation	$=$	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$
Only carbon diffuses during nucleation	$\neq$	$=$	$=$	$=$	$=$	$\neq$	$\neq$	$\neq$
Reconstructive diffusion during nucleation	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$=$	$=$	$=$
Often nucleates intragranularly on defects	$=$	$\neq$	$\neq$	$=$	$\neq$	$\neq$	$=$	$\neq$
Diffusionless growth	$=$	$=$	$=$	$=$	$\neq$	$\neq$	$\neq$	$\neq$
Reconstructive diffusion during growth	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$=$	$=$	$=$
Atomic correspondence (all atoms) during growth	$=$	$=$	$=$	$=$	$\neq$	$\neq$	$\neq$	$\neq$
Atomic correspondence, during growth, for atoms in substitutional sites	$=$	$=$	$=$	$=$	$=$	$\neq$	$\neq$	$\neq$
Bulk redistribution of X atoms during growth	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$\otimes$	$\otimes$	$\otimes$
Local equilibrium at interface during growth	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$\otimes$	$\otimes$	$\otimes$
Local paraequilibrium at interface during growth	$\neq$	$\neq$	$\neq$	$\neq$	$=$	$\otimes$	$\otimes$	$\neq$
Diffusion of carbon during transformation	$\neq$	$\neq$	$\neq$	$\neq$	$=$	$=$	$=$	$=$
Carbon diffusion-controlled growth	$\neq$	$\neq$	$\neq$	$\neq$	$=$	$\otimes$	$\otimes$	$\otimes$
Cooperative growth of ferrite and cementite	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$=$
High dislocation density	$=$	$=$	$=$	$=$	$\otimes$	$\neq$	$\neq$	$\neq$
Incomplete-reaction phenomenon	$\neq$	$=$	$=$	$=$	$\neq$	$\neq$	$\neq$	$\neq$
Necessarily has a glissile interface	$=$	$=$	$=$	$=$	$=$	$\neq$	$\neq$	$\neq$
Always has an orientation within the Bain region	$=$	$=$	$=$	$=$	$=$	$\neq$	$\neq$	$\neq$
Grows across austenite grain boundaries	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$=$	$=$	$=$
High interface mobility at low temperatures	$=$	$=$	$=$	$=$	$=$	$\neq$	$\neq$	$\neq$
Displacive transformation mechanism	$=$	$=$	$=$	$=$	$=$	$\neq$	$\neq$	$\neq$
Reconstructive transformation mechanism	$\neq$	$\neq$	$\neq$	$\neq$	$\neq$	$=$	$=$	$=$

imaginary labeling of the individual atoms) are derived from *corresponding* vectors, planes, and unit cells of the other structure. This is termed a lattice correspondence and it defines a pure lattice deformation which carries the original lattice points, or some fraction of these points, into points of the new lattice. When interstitial atoms are present, they may move over large distances during transformation without affecting the lattice correspondence; this is sometimes loosely expressed by stating that there is an atomic correspondence for the solvent and substitutional solute atoms but not for the interstitial atoms. A further relaxation of the condition is to allow the solvent and substitutional solute atoms to be displaced during transformation among the sites specified by the lattice correspondence, but not to create new sites or to destroy any specified sites; in this way the lattice correspondence is preserved but there is no longer an atomic correspondence. Note that in the classification presented above, the single atomic jumps of interstitial atoms needed to destroy Zener ordering (which is produced automatically by the Bain correspondence) are not taken into account.

Even though two crystals may have an identical *bulk* composition, it may not be concluded that their compositions at the transformation interface are identical. There are modes of transformation (*e.g.*, negligible partitioning local equilibrium) where the bulk compositions are predicted to be identical, but, in the vicinity of the transformation interface, the two phases differ in composition.

For plain carbon steels, there is no difference between equilibrium and paraequilibrium.

The incomplete-reaction phenomenon implies that when a reaction can be studied in isolation, it stops before the phases reach their equilibrium or paraequilibrium compositions when stored energy terms have been accounted for.

An orientation within the Bain region means a reproducible relation which may be irrational but is close to the rational NW or KS relation.

Massive ferrite is not classified as a separate morphology since it can be included within allotriomorphic or idiomorphic ferrite.

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