A Debate on the Bainite Reaction

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The authors debate three topics central to the controversies which have enveloped the bainite reaction ever since it was first recognized as a distinctive mode of austenite decomposition. These include: "what is bainite?", "the growth mechanism of the ferritic component of bainite", and "the sources of bainitic carbide precipitation." RFH concludes that bainite is the product of a shear transformation. Individual bainite plates are suggested to grow substantially more rapidly than volume diffusion-control allows, but a constraint such as the build-up of volume strain energy limits the extent of their growth. This mechanism of growth ensures extensive supersaturation of bainitic ferrite with respect to carbon. Whether or not carbides precipitate in association with bainite plates and whether the carbide is cementite or ϵ , however, is a complex question in competitive reaction kinetics. New experimental evidence is presented to demonstrate that ϵ carbide precipitated in lower bainite dissolves upon heating above the kinetic- B_s temperature in an alloy steel containing 1.5 pct Si. This result is taken to support the existence of the metastable eutectoid reaction $\gamma \rightleftharpoons \alpha + \epsilon$ at *ca* 350°C. HIA and KRK define bainite as the product of a nonlamellar eutectoid reaction. On this view, carbide precipitation thus plays an essential, rather than an ancillary role. Development of the Widmanstatten morphology by the ferritic component of bainite is shown to be inessential to the classification of a eutectoid structure as bainite. When this morphology is present, however, it is concluded to grow by the ledge mechanism, without the participation of shear, at rates of the order of or less than those allowed by volume diffusion-control. New experimental evidence is presented to show that the lengthening and thickening kinetics of individual plates within sheaves of upper bainite are consistent with this description. The results of a new calculation indicate that the initial carbon content of bainite plates lies between the $\alpha/(\alpha + \text{Fe}_3\text{C})$ and the extrapolated $\alpha/(\alpha + \gamma)$ phase boundaries, in agreement with expectation from the ledge mechanism of growth.

 \mathbf{O} N the occasion of his 80th birthday, it must be a source of both pleasure and frustration to Dr. Edgar Collins Bain to observe that the phase transformation named in his honor continues to be the subject of so much research throughout the world, and yet remains so controversial that, more than 40 years after its discovery, almost the only aspect of it upon which there is general agreement is that still more research is needed! In the hope of encouraging a more focussed effort to resolve these controversies, the present authors have selected the three issues which they consider to form their core and have engaged in a debate upon them. In respect of the first issue, that of answering the question "what is bainite?", the two sides (RFH on one; HIA and KRK on the other) exchanged statements of position and then two further rounds of rebuttal. Considerations of length restricted debate on the other two topics, "the growth mechanism of the ferritic component of bainite" and "the sources of bainitic carbide precipitation", to two exchanges on each. No substantial alterations were subsequently made in these exchanges. Not surprisingly, the level of agreement reached was sufficiently modest so that for the Summary section the views of the two sides were again separately prepared. The basic nature of the problems involved, however, appears to have been clarified, and as a result the paths which future experimental and theoretical studies might most profitably follow now seem to be better illuminated.

TOPIC I: WHAT IS BAINITE?

R. F. H. (Round 1)

The term bainite refers to the acicular decomposition products that form when austenite is transformed at intermediate temperatures. The similarities between bainite and martensite on the one hand and between bainite and Widmanstatten ferrite on the other have been recognized since the pioneering work of Davenport and Bain¹ and have resulted in several divergent views of the reaction mechanism. The many problems that have prevented delineating this mechanism unambiguously have recently been reviewed critically.²

The formation of bainite constitutes a complex problem in competitive reaction kinetics involving the allotropic transformation of γ to α , partition of carbon between these phases, precipitation of cementite (and other carbides) from ferrite and/or austenite as well as accommodation and relaxation of transformation strain. Until the reaction mechanism is more clearly established in terms of the interplay of these processes, it appears to be necessary to define bainite in terms of its structural as well as kinetic features. Three characteristics appear to be significant:

1) Microstructure—In the steels of greatest interest, the carbon content exceeds that for the solubility of carbon in ferrite. Under these conditions, bainite is a nonlamellar aggregate of ferrite and carbide with an acicular morphology dictated by the ferritic component. At least two and possibly a greater number of variants of bainite are recognized. The classical variants encompass the feathery structure known as upper bainite and the plate-like product known as lower bainite.³ Both forms are nucleated by ferrite⁴ and, although the structures have been characterized in

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detail,^{5,6} the reason for their difference is not yet clearly established.

2) Surface Relief-Growth of bainite takes place slowly and formation of both upper and lower bainite is accompanied by surface relief.⁷⁻¹⁰ In addition, the crystallographic features of lower bainite are specified adequately by the phenomenological theories of martensite reactions.¹¹ The similarity between the crystallography and surface relief of upper bainite and that of low-carbon martensite also has been emphasized.⁶ This has led to the concept that bainite is a displacive transformation controlled by the rate at which composition change is accomplished by removal of carbon to the surrounding austenite.^{12,13} This conclusion is not yet universally accepted and the observation that Widmanstatten ferrite also exhibits relief¹⁴ has led to alternate interpretations of the relief. These disagreements coupled with those on other experimental observations are at the heart of the confusion surrounding the reaction mechanism.

3) Reaction Kinetics—In alloy steels, an upper temperature, designated B_s , exists above which austenite will not transform by the bainitic mode. Below this temperature, bainite forms relatively rapidly, but, near B_s , transformation stops before all of the austenite has been transformed.¹⁵ The amount of austenite transformed to bainite increases as the reaction temperature is lowered. In plain carbon steels, these kinetic aspects of the reaction are obscured by competition from the pearlite and proeutectoid reactions. In spite of these observational difficulties these features appear to be common to the bainite reaction in plain carbon as well as alloy steels.

H. I. A. and K. R. K. (Round 1) $\mathbf{1}$

Most physical metallurgists are likely to agree with the view¹⁶ that a question such as this is best answered on the basis of the fundamental mechanism of transformation. However, it has been recently pointed out that three quite different answers to this question are now available in the literature, each of which centers about a different transformation mechanism:²

1) The Microstructural Definition—Based primarily upon the pioneering studies of Robertson¹⁷ and of Davenport and Bain,¹ and much reenforced by the subsequent work of Hultgren,^{4,18} this definition considers bainite to be a dispersion of nonlamellar carbides formed in association with proeutectoid ferrite, *i.e.*, the product of a nonlamellar eutectoid reaction. The previously accepted restriction that the ferrite phase have a Widmanstatten morphology has been shown to be unnecessary.² On this definition, the distinguishing fundamental mechanisms of transformation are carbide precipitation within ferrite and at austenite:ferrite boundaries.

2) The Kinetic Definition—Due largely to Wever and Lange,¹⁹ this definition is couched in terms of the overall kinetics of transformation: the bainite reaction has its own C-curve; as the maximum temperature of this curve (the "kinetic- B_s ") is approached, the proportion of bainite formable decreases (ideally) to zero. Many mechanisms have been proposed for these phenomena;² most recently, it was suggested that a solute drag-like effect of alloying elements which strongly decrease the activity of carbon in austenite is primarily responsible. $^{2_{320,21}}$

3) The Surface Relief Definition—Originally developed by Ko and Cottrell,^{7,22} this definition currently considers to be bainite any slowly growing precipitate plate which produces a martensitic surface relief effect. The basic mechanism proposed is growth by shear at rates determined by long-range solute diffusion.

The following items illustrate the substantial conflicts which exist among these definitions. Surface relief vs microstructural: surface relief bainite can form above the eutectoid temperature.^{22,23} Surface relief vs kinetic: the W_s (Widmanstatten-start) or surface relief- B_s temperature lies as much as 200°C above the kinetic- B_s in 0.1 pct C Fe-C-Mo and Fe-C-Cr alloys.²⁴ Microstructural vs kinetic: microstructural bainite can form both above and below kinetic- B_s in Fe-C-Cr alloys.^{2,25} Poor agreement between kineticand microstructural- B_s is also found in Fe-C-Mo alloys.²

The kinetic definition of bainite is readily eliminated on the ground of lack of generality. The absence of incomplete transformation (defined as a smaller proportion of ferrite than that allowed by the Lever Rule) at temperatures just below the kinetic- B_s has been recently demonstrated in Fe-C-2 pct Mo alloys of varying carbon content.²¹ The "bay" in the *TTT*-diagrams of these alloys was shown to result from a minimum in the growth kinetics of ferrite at this temperature.²¹ No such minimum in ferrite or bainite growth kinetics appears in steels which do not show a bay.¹³ Thus the phenomena associated with the kinetic definition are insufficiently general to warrant an appellation as broad in scope as that of "bainite".

The bainite photographed by Robertson¹⁷ and by Davenport and Bain¹ consists largely of a dispersion of nonlamellar carbides in Widmanstatten ferrite. The present, generalized microstructural definition eliminates the requirement that the ferrite appear in a Widmanstatten morphology, whereas the surface relief definition proposes that the presence of carbides is inessential. A decision as to which of these definitions is more appropriate can be made, however, on the basis of reaction mechanism. When the surface relief aspect of the subsequently developed phenomenological theory of martensite 26,27 is applied to make the original Ko-Cottrell⁷ definition more rigorous, the ferritic component of bainite must be a plate in three dimensions, not a needle, and the relief effect must be an invariant plane strain.^{28,29} Proeutectoid ferrite and upper bainite, however, often appear as needles.^{30,31} Widmanstatten ferrite sometimes yields an invariant plane strain relief,²⁹ but "vee"- or "tent"-shaped relief morphologies are often observed in association with single crystals of both ferrite^{2,32} and lower bainite.³³ These incompatibilities between definition and experiment provide a good indication that the fundamental transformation mechanism upon which the surface relief definition rests is, in fact, not operative during the formation of bainite in steel. Although plates of α brass precipitated from β do satisfy the relief effect specifications of the phenomenological theory,^{29,34} data on their lengthening kinetics indicate that at least some zinc partition occurs between α and

 β during growth.^{*35} No solute partition at all is admis-

sible, however, in a substitutional solid solution undergoing a shear transformation.²⁸ It is thus recommended that the surface relief definition of bainite be discarded.²

The microstructural definition, on the other hand, is in good accord with the phenomena which it describes. Although there is a peripheral tendency for merger with pearlite,^{39,40} the microstructural bainite reaction not only in steel but in such diverse alloy systems as Fe-N,⁴¹ Ti-Cr,⁴² and Cu-Al and Cu-Sn⁴³ is clearly the nonlamellar eutectoid transformation required by the definition. Terming such a reaction "bainite", and considering it, with Hultgren,^{4,18} to be the nonlamellar counterpart of pearlite, is accordingly recommended as the answer to the question "What is bainite?".

R. F. H. (Round 2)

The microstructural, kinetic, and surface relief phenomena are basic characteristics that must be explained by the correct mechanism and should not, in my opinion, be viewed as independent or mutually exclusive definitions.

<u>1) Microstructure</u>—To consider bainite exclusively to be a nonlamellar ferrite-carbide aggregate without regard to kinetic and other features of the transformation excludes single phase decomposition products and incorporates some aggregate structures that otherwise may not be closely related mechanistically. The latter applies particularly to alloy carbides precipitated from proeutectoid ferrite formed at temperatures near or above A_1 .²

Very low carbon Fe-Ni alloys exhibit a "slowly" growing product that develops with surface markings essentially the same as that for the martensitic structure formed at lower temperatures.^{44,45} Although single phase, these structures appear to be closely related to the bainitic structures produced in steels of comparable nickel but higher carbon content. The kinetic and surface relief characteristics indicate that these structures can potentially be viewed as bainite. The observation of several thermal arrests in high-purity iron also has been interpreted in terms of a bainitic reaction in pure iron.⁴⁶

As mentioned by Drs. Kinsman and Aaronson, α plates formed by low temperature aging of β brass represents another transformation excluded from consideration as bainite because it is single phase. The ability of external stress to selectively favor certain variants of the product has been attributed to a shear component of the transformation strain.^{*47} Similar re-

*Nonbainitic products in other systems did not exhibit this selectivity although nucleation was enhanced.

sults are observed in the formation of $bainite^{48}$ in steels and imply that a shear reaction is involved in both cases.

2) Surface Relief—The displacive character of the surface relief associated with lower bainite has been carefully established¹¹ as has the close connection between the crystallography and substructure of upper bainite and low-carbon martensite.^{5,6} Ferrite laths

constitute the basic unit in both upper bainite and lowcarbon martensite. Since low-carbon martensite itself is not well understood in terms of the phenomenological theories, there does not yet appear to be sufficient grounds to reject the concept that a displacive reaction is involved in the formation of either upper or lower bainite.

"Vee"- or "tent"-shaped relief also does not exclude a shear mechanism for the transformation. This may arise simply from the juxtaposition of two variants of the transformation product.²⁹ However, in the case of lower bainite, it has been shown⁴⁹⁻⁵¹ that these plates frequently thicken from one side only. In this case, such plates exhibit a "tent" relief in which the apex of the tent is one edge of the plate. One-half of the tent then represents austenite deformed by slip or kinking as has been suggested by Christian.²⁸ The asymmetric growth and its relation to the relief has been confirmed by etching of samples after recording the relief by hot-stage metallography.⁵² Klosterman¹³³ has observed similar unidirectional thickening of surface martensite and has proposed that a plate "will broaden only in the direction for which the shape deformation promotes a hydrostatic tensile stress." It should be noted, however, that other studies³³ have shown that both sides of the tent can consist of the transformation product.

3) Kinetics—The concept that B_s results from a special effect of alloying elements on the growth of proeutectoid ferrite²⁵ is extremely attractive and emphasizes the question of whether or not a B_s temperature exists in plain carbon steels. This is a difficult question to answer experimentally; however, it has been suggested that B_s in these materials can be identified with a difference in substructure between Widmanstatten ferrite and bainite.⁴⁹ There appears to be at least a discontinuous change in the autocatalytic contribution to nucleation at B_s and this may signify a change in the mode of relaxation of accommodation strains.

It also seems advisable to distinguish between products formed at the same temperature but at different rates. Three pct Cr steels containing 0.08 pct to more than 1 pct C exhibit an initial rapid reaction that transforms only a limited amount of the austenite at temperatures near B_s .²⁵ The remaining austenite subsequently transforms at a much lower rate. At carbon levels above approximately 0.4 pct this involves separate ferrite and carbide reactions; however, at the lower carbon levels it is difficult to distinguish metallographically between the product of the initial rapid reaction and the subsequent much slower reactions. Nevertheless, the kinetic results suggest that a fundamental difference exists between the two products.

The existence of a "kinetic- B_s " and a rapid incomplete reaction (decreasing to 0 pct at B_s and thus much below amounts permitted by the lever rule) also occurs in steels alloyed with elements such as silicon⁵³ and nickel^{54,55} which increase the activity of carbon in austenite. This phenomenon is more general than is permitted by the solute drag model in its present form.

H. I. A. and K. R. K. (Round 2)

In answering the question "what is bainite?", Prof. Hehemann:

1) Accepts the classical microstructural definition of

^{*}The recent analysis of Purdy³⁶ implies a considerably closer approach to equilibrium levels of partition. Electron probe indications to the contrary³⁷ are probably incorrect.³⁸

bainite, in which only the acicular morphology of the ferritic component is allowed.

We are in agreement in requiring that the ferrite contain a nonlamellar dispersion of carbides in order that the resultant aggregate structure warrant classification as bainite, but not in restricting the morphology of the ferrite phase to the acicular form. Both in the present debate and in his recent detailed review of the bainite reaction,⁵³ Prof. Hehemann prefers to confine attention to "the two classical variants of bainite", namely upper and lower bainite. Use of the term "classical" in this context of implied soundness seems an inappropriate reason, however, for omitting major items of (admittedly inconvenient) experimental evidence. This debate is being held primarily because the classical views have led to intolerable confusion. We therefore recall attention to the existence of the following nonacicular morphologies of the ferritic component of bainite:

a) Columnar bainite-observed in both carbon and alloy steels at atmospheric^{9,56-58} and high^{59,60} pressures.*

*The suggestion that columnar bainite should be ignored because it may result from the operation of another mechanism of ferrite formation⁵³ seems overdrawn; development of the various morphologies of proeutectoid ferrite, for example, involves a considerable variety of transformation mechanisms.^{30,61}

b) Granular bainite—reported in isothermally transformed plain carbon⁶² and nickel⁶³ steels with lowcarbon contents.*

*Hehemann⁵³ points out that Habraken^{65,66} originally observed granular bainite primarily in continuously cooled specimens, and more importantly, often found this structure to be essentially free of carbides. The latter circumstance, on both our views, would prevent classification as bainite. However, the presence of carbides in granular bainite was established by transmission electron microscopy in nickel steels.⁶³

c) Bainitic grain boundary allotriomorphs—these are observed in small amounts in coarse grained hypoeutectoid steels;^{2,66} greatly reducing the austenite grain size, however, can make them the predominant morphology at reaction temperatures and times which yield (in the same steel) coarsely acicular bainite when the austenite grain size is large.² Allotriomorphs are probably often the "unit" morphology of granular bainite.⁶³ They are evidently also the major ferrite morphology in the bainite which Davenport, Berry, and Honeycombe⁶⁷ describe as the product of "interphase precipitation" of carbides at austenite:ferrite boundaries in Fe-C-X alloys when X is a substitutional alloying element with a strong tendency for carbide formation.

This evidence for nonacicular morphologies of the ferritic component of bainite seems sufficiently substantial so that it should not be ignored in attempting to develop a better definition of bainite.

2) Accepts the mechanistic basis of the surface relief definition, *i.e.*, that the acicular ferrite portion of bainite forms by shear (we shall take issue with the crystallographic and surface relief arguments which he uses to support this conclusion under Topic II), but apparently rejects in at least one important case a logical consequence of this definition by declining to classify carbide-free Widmanstatten ferrite as bainite. Unfortunately, he recently appeared to accept this consequence in another alloy system by classifying as bainite acicular α precipitated from β Cu-Zn.⁵³ In such alloys, of course, there is no eutectoid reaction. We would appreciate an explicit resolution of this apparent conflict.

3) Accepts the view that the ferritic component of bainite contains a higher than equilibrium proportion of carbon. If this is advanced as an essentially independent and fundamental characteristic of bainite, as Le Houllier, Bégin, and Dubé⁶⁸ are currently doing, then a substantial new level of complication is introduced. Clearly, a nonlamellar eutectoid can be generated by carbide precipitation from ferrite and/or from austenite (the latter at austenite:ferrite boundaries) even though the carbon content of the ferrite does not exceed that of the extrapolated $\alpha/(\alpha + \gamma)$ curve. On the other hand, if this point is essentially a corollary of the Oblak-Hehemann⁴⁹ rapid growth mechanism of bainitic ferrite formation, discussion of it can be deferred to Topic II.

4) Accepts the kinetic definition of bainite. Although Oblak and Hehemann⁴⁹ have found steels in which ferrite morphology changes from Widmanstatten ferrite to upper bainite at the kinetic- B_s ,* clear examples of

*Unless bainitic carbides began to form at this temperature, it was not also the microstructural- B_s .

noncorrelation between the microstructural- and the kinetic- B_s temperatures have been reported² and are noted in our first presentation on this topic, indicating that the two temperatures are not, in general, identical. Boswell *et al.*²¹ have shown that incomplete transformation^{*} does not occur near the kinetic- B_s in several

*They define this as less ferrite than that allowed by the Lever Rule.

low-carbon Fe-C-2 pct Mo alloys. They also point out²¹ that the dilatometric results of Lyman and Troiano²⁵ on Fe-C-3 pct Cr alloys, allegedly showing extensive incomplete transformation, correlate badly with the microstructural observations on these alloys; the latter are qualitatively but nonetheless quite clearly indicative of the same behavior as is exhibited by the Fe-C-2 pct Mo alloys.

R. F. H. (Round 3)

The nonlamellar nature of bainite presumably implies that a lower degree of cooperation is involved in the formation of ferrite and carbide here than in pearlite.⁴⁰ This cooperation, however, may play no direct role in the reaction mechanism, influencing only the gross microstructure. It is especially not clear that a carbide phase need be present. For example, upper bainite in silicon steels is free (or nearly so) of carbide.4,49,60 Presumably, this results from the ability of silicon to retard the precipitation of cementite from ferrite and austenite and this will be considered further in Topic III. Although single phase, these structures are bainites in my opinion. The high-purity Fe-Ni alloys mentioned in Round 2 as well as the granular bainites described by Habraken⁶⁵ also fall in this category. He has shown that these structures form in an "athermal" manner below a B_s temperature (near 550°C) and exhibit the lath substructure of upper bainite and low-carbon martensite. Carbides may be present when the structure is formed at sufficiently low cooling rates but their absence in structures formed at higher cooling rates does not exclude classification as bainite.

The nonacicular nature of granular bainites results from impingement and this, I believe, also is responsible for the nonacicularity of upper bainite formed in fine-grained austenite.² For example, we have observed surface relief in upper bainite formed over the austenite grain size range from ASTM 8 to 0. In agreement with Aaronson,² the bainites formed in the finegrained austenite were nonacicular but this results from impingement rather than conversion to an allotriomorphic morphology. I am willing to remove the restriction of acicularity from the gross microstructure but do not agree that this implies allotriomorphic growth. Thus, those nonlamellar aggregates formed by precipitation of alloy carbides from allotriomorphs formed at high temperatures are not, in my view, bainite and this includes the structures reported by Berry *et al.*⁷⁰

To be more specific, it is my opinion that bainites involve a correspondence and a shear transformation that is analogous to that involved in martensitic reactions. The growth of bainite is thermally activated, but it is not clear to me whether this arises from composition change or from other processes. These points, including the question of initial supersaturation of ferrite, will be considered under Topics II and III.

In the above considerations, attention has been focussed on the ferritic component of bainite and carbide precipitation has been viewed as a secondary process as has been done by others.¹³ Within this framework single-phase products are not excluded provided that they exhibit a shear transformation. This appears to be the case for the low-temperature plates formed in β brass³⁴ which I would consequently classify as bainitic. If it is shown in this debate or subsequently that Widmanstatten ferrite and bainite form by the same mechanism—shear or otherwise—then a distinction between them may no longer be necessary.

Two other points raised by Drs. Kinsman and Aaronson in Round 2 require some response. Unfortunately, with regard to columnar bainite, I have no comments beyond my previous statements.⁵³ At present it is not known whether these structures form by the same mechanism as the conventional bainites. Finally, with regard to the work of Boswell *et al.*, I emphasize again that a clear refutation of the observation that two kinetically different products²⁵ have *not* formed in their experiments is needed.

H. I. A. and K. R. K. (Round 3)

Both the first sentence of Professor Hehemann's Round 2 of this Topic and the first paragraph of his Round 1 implicitly recognize the existence of serious conflicts among the various definitions, but a resolution of this difficulty is not yet proposed. Thus, in connection with the kinetic definition of bainite we are urged to accept the view⁴⁹ that *in these materials* (the steels used by Oblak and Hehemann) bainite consists of sheaves of Widmanstatten ferrite plates. Further definitional conflict is generated in the fourth paragraph of his Round 2, in which he accepts as bainite low-temperature α -brass precipitates, which usually appear as single plates.³⁵ A definition of a phase transformation which varies with the alloy system to which it is applied does not appear to be particularly useful.

A careful reading of Prof. Hehemann's Rounds 1 and 2 suggests that he considers the presence of nonlamellar carbides to be an important characteristic of bainite *in many steels*, but perhaps not so important that this must constitute an element of the *definition* of bainite. He appears, however, to be much more firm in accepting the surface relief definition of bainite. A preliminary statement of our objections to this definition was given in Round 1.

Concerning the concept that the phenomena associated with the kinetic definition of bainite are a special effect of certain alloying elements upon the proeutectoid ferrite reaction:²⁰ "the initial rapid reaction and the subsequent much slower reactions" of which Prof. Hehemann writes are not a characteristic of the many Fe-C alloys which the present authors have examined in the bainite range.

Concerning "the ability of external stress to selectively favor certain variants of the product", which is attributed to a "shear component of the transformation strain" associated with bainite: the stresses associated with a dislocation favor certain habit planes during a number of precipitation reactions (Table II of Ref. 71). Particularly when the matrix is a solid solution and the product is an intermetallic compound of markedly different composition, the transformation mechanism cannot be one of shear.

Despite the complexity of this field, we feel that sufficient knowledge is now available to allow the formulation of a material-independent, substantially conflictfree *definition* of bainite. Our arguments have been to the end that the generalized microstructural definition (bainite is the product of the nonlamellar mode of eutectoid decomposition) best fulfills this specification.

TOPIC II: THE GROWTH MECHANISM OF THE FERRITIC COMPONENT OF BAINITE

R. F. H. (Round 1)

Many studies^{5,6,72} have shown that bainite exhibits a lath-like substructure with thickness $<1 \mu$, width 5 to 10μ and variable length but frequently in the range from 10 to 50μ . This substructure is basically the same as that in low-carbon martensite as is the nature of the surface relief and crystallography of the ferrite in upper bainite. Optical metallography⁴⁹ suggests that these subunits are the basic growth units of bainite; *i.e.*, the substructure does not appear to result from deformation or recovery processes subsequent to its growth. There also appears to be a significant shear strain involved in the transformation as indicated, for example, in the ability of external stress to selectively favor specific variants of the transformation product.⁴⁸

Although direct proof that an invariant plane strain is involved in the formation of upper bainite is not yet available, these subunits are considered to form by a cooperative transfer of lattice atoms though not necessarily at the rate characteristic of martensitic reactions. The alternative is that the individual units grow by a ledge mechanism⁶¹ and that impingement produces the arrangement characteristic of upper bainite. If Widmanstatten ferrite and upper bainite are indeed continuous as has been suggested^{7,13,40} then a distinction between them may be artificial.

Several observations suggest that basic differences exist between upper bainite and Widmanstatten ferrite:

1) When growth of bainite in alloy steels stops, the

outermost laths are in contact with austenite but do not continue to thicken as would be expected from the ledge mechanism.

2) The Widmanstatten ferrite concept provides no obvious clue concerning the rather sudden appearance of sympathetic nucleation⁷³ in a rather critical temperature range associated with the kinetic B_s .⁴⁹ The self-accommodating nature of low-carbon martensite, on the other hand, provides a ready explanation.

The transition from ferrite to bainite may arise primarily from differences in the way in which transformation strains are relaxed. Specifically, at high temperatures, diffusional processes (e.g. creep) may relax stresses before slip processes become operative. As diffusion rates are lowered by reduction in temperature, a point is reached at which stresses become high enough to initiate slip. The principal point is that a critical condition appears to be fulfilled at B_s which signals initiation of the bainite range. In these terms, B_s need not correlate directly with T_0 provided only that B_s be less than T_0 if bainite is to form with the full supersaturation of the parent austenite.

It is firmly established that growth of bainite is thermally activated. Generally, this has been interpreted in terms of a shear transformation that propagates at a rate controlled by diffusion of carbon into the surrounding austenite.²⁸ Growth rates calculated from these models agree well with experimental measurements in plain carbon steels⁷⁴ and it has recently been shown that the lower growth rates of bainite in alloy steels also agree with calculations based on these local equilibrium concepts.⁷⁵

While it is difficult to argue against these diffusion controlled models, other thermally activated processes could, in principle, control growth. In this event, partition of carbon should occur to an extent permitted by the growth rate rather than dictating the growth rate. The experimental question here concerns the significance of growth rate measurements made with the hotstage microscope. We have suggested that these measurements refer to a repeated nucleation process and that individual subunits may grow at a relatively high rate to some limiting size.⁴⁹ Alternatively, the concept that a diffusionless transformation can grow continuously at a low rate controlled by a balance of the net driving force with a frictional force has recently been developed in detail.⁷⁶ At carbon contents below 0.1 pct, this model also predicts growth rates comparable to those observed experimentally.

The process envisioned here does not rely directly on cooperative growth of ferrite and carbide. Thus, carbide precipitation is viewed as a secondary process that may influence the overall microstructure but affects the growth process in only an indirect way.

H. I. A. and K. R. K. (Round 1)

Despite our adherence to the generalized microstructural definition of bainite, in which no restriction is placed upon the morphology of the ferritic component, for the purposes of the debate on this Topic we shall assume that this morphology is exclusively of the Widmanstatten type to assure "coherency" with the considerations of Prof. Hehemann. We shall place primary emphasis upon growth kinetics, but will also consider the crystallography of the ferritic component of bainite.

Emphasizing the results on high-purity Fe-C alloys, data on the lengthening kinetics of ferrite plates are available in the proeutectoid ferrite and upper bainite regions in hypoeutectoid alloys^{13,77-79} and in the lower bainite region in hypereutectoid alloys.⁹ Since we now know that the inverse bainite³⁹ reaction does not extend below ca 475°C in hypereutectoid Fe-C alloys, independently of composition,⁸⁰ both sets of data may be considered together. Employing the sophisticated analysis of plate lengthening due to Trivedi,⁷⁴ Simonen *et al.*⁷⁹ recently concluded that, contrary to previous results,^{13,79} the lengthening mechanism in the proeutectoid ferrite and upper bainite regions is controlled by the formation and lateral movement of ledges. Since the other lengthening rate data in hypo- and in hypereutectoid alloys are consistent with those of Simonen et al., it is not unreasonable to conclude at least tentatively that this mechanism of lengthening is applicable throughout the bainite range. The only extensive data on Widmanstatten thickening kinetics in Fe-C alloys which were obtained (via thermionic emission microscopy) with sufficient resolution in time and space are those of Kinsman $et \ al.^{32}$ on proeutectoid ferrite plates. In several instances, the ledge mechanism of thickening was observed directly while growth was in progress. With the aid of the Jones-Trivedi⁸¹ analysis of ledge growth, however, the much larger amount of data obtained on the overall kinetics of thickening were used to calculate the average spacing between ledges. The finding that these spacings are in acceptable agreement with those measured by means of electron microscopy strongly supports the ledge mechanism originally proposed⁶¹ for the thickening of ferrite plates, and indicates that the rate of lengthening of the ledges is controlled by the volume diffusion of carbon in austenite. These results have been shown to rule out a variety of shearbased growth mechanisms.²

In the upper and lower bainite regions, the ferrite plates are grouped in sheaves⁴⁹ as a result of sympathetic nucleation at the broad faces of these plates.⁷³ Measurement of the lengthening, and especially of the thickening kinetics of individual plates (termed "subunits" by Oblak and Hehemann⁴⁹) in these sheaves is a difficult problem because of the high resolution required. However, these measurements must nonetheless be attempted in order to test critically the following mechanism which Oblak and Hehemann have proposed for the growth of bainite sheaves. Individual plates in the sheaves are postulated to grow by shear at high rates, not necessarily of sonic velocity, but much faster than would be possible if equilibrium partition of carbon between austenite and ferrite were to occur continuously during growth. Growth was further suggested to proceed only to a limiting size, of the order of 10 μ m in length and 0.5 to 0.7 μ m in thickness, and then to halt as a consequence of some factor such as accumulated volume strain energy. On this mechanism, the growth rates of sheaves reported in the literature are primarily a measure of the rate of sympathetic nucleation. Although the resolution of hot-stage optical microscopy is apparently insufficient to test this mechanism, Oblak and Hehemann⁴⁹ have suggested that thermionic emission microscopy may have the

requisite capability. Using motion pictures which Rouze and Grube^{82,83} took of the bainite reaction with this type of microscopy, we have found that the technique does have the necessary resolution.

Using an automated version of the Vanguard Motion Analyzer, considerable data on the lengthening kinetics of individual plates or "subunits" in sheaves of upper bainite plates formed at 400°C in an Fe-0.66 pct C-3.32 pct Cr alloy were obtained from these films. Figs. 1(a)to 1(c) show length vs time plots of individual "subunits" in the sheaf illustrated in Fig. 1(d). Although the smallest growth distance between the data points in these graphs is $ca \ 3 \ \mu m$, this could have been reduced by a factor of four simply by measuring each frame. It was, however, always entirely clear that individual subunits lengthened continuously at rates essentially the same as that of the sheaf as a whole. The approximately 10 μ m long "jumps" in length which Oblak and Hehemann postulated to occur at rates far more rapid than the overall lengthening rate of a sheaf were never observed. Figs. 2(a) and 2(b) show similar plots for the smaller sheaf of Fig. 2(c). The plate whose kinetics are reported in Fig. 2(a) is the leading component of a sheaf; it has essentially the same rate of lengthening



as the individual plates in the sheaf in Fig. 1. The average lengthening rate of the plates in Figs. 1(a) to 1(c) and Fig. 2(a) is $ca 1.4 \times 10^{-3}$ cm/sec. This is in reasonable agreement with the lengthening rate, ca 9×10^{-4} cm/sec, which KRC¹³ extrapolated to this temperature from the data of Hillert⁷⁷ on a 0.59 pct C plain carbon steel. Calculation of the influence of chromium upon the extrapolated Ae3 presents substantial problems;⁸⁴ however, from the effects of chromium upon the equilibrium Ae3 curve, the change in lengthening rate is in the correct direction. Since Hillert's data are consistent with those of Simonen $et \ al.,^{79}$ it seems reasonable to conclude that the subunits in the bainite sheaves investigated also lengthen by the formation and the diffusion-controlled lateral movement of ledges.

Obtaining measurements of the thickening kinetics of individual subunits within sheaves proved to be just within the limit of resolution of the Rouze-Grube films.



Fig. 1-Lengthening kinetics (a) to (c) of individual plates or "subunits," identified by arrows, in the sheaf of upper bainite illustrated in the thermionic emission electron microscopy ciné sequence in (d). Isothermal transformation at 400° C of a Fe-0.66 pct C-3.32 pct Cr alloy.

Fig. 2—Lengthening kinetics (*a*) to (*b*) of individual plates or "subunits," identified by arrows, in the sheaf of upper bainite illustrated in the thermionic emission electron microscopy ciné sequence in (*c*). Isothermal transformation at 400°C of a Fe-0.66 pct C-3.32 pct Cr alloy.



Fig. 3—Thickening kinetics of an individual subunit in a sheaf of upper bainite obtained in an Fe-1.04 pct C-6.1 pct Mn-0.97 Mo alloy isothermally transformed at $371^{\circ}C$.

Fig. 3 shows one of the better results obtained, in an Fe-1.04 pct C, 6.1 pct Mn, 0.97 pct Mo alloy. Oblak and Hehemann⁴⁹ found, by means of transmission electron microscopy, that the individual plates or subunits within sheaves are of the order of 0.5 to 0.7 μ m wide. The sums of the discontinuities in this plot (indicated by dashed lines, marked a and c, and representing the passage of a partially thickened subunit), and of the additional thickening which followed immediately thereafter (denoted by solid lines, marked b and d) are $a + b = 1.0 \,\mu\text{m}$ and $c + d = 0.7 \,\mu\text{m}$, respectively. These plate widths are in adequate agreement with the electron microscopy observations. Assurance is thus given that we are observing the thickening of an individual subunit. Inserting the measured thickening rate (ca $0.006 \,\mu m/sec$ in both regions of thickening) in the standard equation for growth by a planar ledge mechanism,⁸⁵ calculating the ledge velocity according to the equation of Jones and Trivedi,⁸¹ and adjusting the value of the extrapolated no-partition Ae3 curve for the effects of the manganese and molybdenum⁸⁴ yields a calculated interledge spacing of $ca 0.5 \,\mu\text{m}$. This is consistent with the 0.3 to 8 μ m range obtained for the early stages in the thickening of proeutectoid ferrite plates in Fe-C alloys.³² Despite the differences in temperature and composition between the two sets of experiments, reasonable concordance between their interledge spacings is to be expected, primarily be-cause electron probe analysis³² and the present lengthening kinetics study indicate that in both cases the growing plates are essentially carbon-free ferrite. One may thus conclude that the thickening of subunits also takes place by the formation and lateral, diffusioncontrolled migration of ledges. Both the lengthening and the thickening results are in clear-cut disagreement with the high-velocity shear mechanism of Oblak and Hehemann.

We shall conclude this presentation with a review of certain crystallographic evidence on the hypothesis that the ferritic component of bainite grows by shear. The conventional wisdom in this area is that of Christian.²⁸ Viewing upper bainite as containing little if any excess carbon and lower bainite as being extensively supersaturated with respect to carbon, Christian suggested that upper bainite ought to have the crystallography of low-carbon martensite whereas lower bainite should exhibit essentially the crystallography of martensite in the same alloy. However, Bowles and Kennon⁸⁶ were not able to understand the crystallography of upper bainite in terms of the phenomenological theory of martensite. Edwards and Kennon⁸⁷ found that in a plain carbon 1.44 pct C steel both the habit plane and orientation relationships of bainite and martensite formed in the vicinity of M_s are quite different. For example, the habit plane of martensite is near $\{225\}_{\gamma}$, whereas that of lower bainite is close to $\{110\}_{\gamma}$. Srinivasan and Wayman,¹¹ investigating lower bainite in an Fe-1 pct C-8 pct Cr alloy, were able to fit the observed crystallography with the phenomenological theory, but only by assuming a value of the dilatation parameter which resulted in a uniform 1.2 pct contraction of the ferrite lattice. The sense of this volume change is opposite to that of the transformation, and especially is the reverse of that accompanying the formation of martensite. The physical significance of the fit obtained with martensite theory thus remains uncertain. Srinivasan and Wayman also found that the orientation relationships and habit plane of lower bainite are different from those of martensite in the same alloy.

These considerations support our view that neither upper nor lower bainite forms by a martensitic mechanism.

R. F. H. (Round 2)

The crystallographic aspects have been considered briefly under Topic I. It appears to be well-established that lower bainite does develop by shear¹¹ and the difference in habit plane between lower bainite and martensite in the same steel must be anticipated from the crystallographic theory. In particular, transmission microscopy^{5,11,88} reveals that different inhomogeneous strains are involved in the formation of the two products and significant relaxation of accommodation strains has been noted in the formation of bainite.¹¹ In particular, lower bainite appears to be free of the internal twins that constitute the inhomogeneous strains in martensite formed in the same steel. Since the habit plane is sensitive to the operating modes of inhomogeneous strain, the difference in habit plane between lower bainite and martensite is consistent with a displacive mode of formation for both reactions.¹¹ Similar considerations may apply to upper bainite and low-carbon martensite. However, the experimental data do not yet appear to be sufficiently complete to decide whether or not the two products exhibit the same crystallographic features or inhomogeneous strains.

The measurements of the Rouze and Grube films demonstrate that growth of upper bainite does not occur discontinuously in increments of rapid growth involving steps of 10 μ m or more in length. However, one reservation must be held. The lath structure of upper bainite indicates that growth increments of this magnitude should only be observed when the lath lies in the plane of polish. For other relative orientations, the substantially smaller growth steps may not be resolved. Several plates in the Rouze-Grube films exhibit nonuniform growth and frame by frame measurements (10/sec) reveal occasional growth increments between frames that occur at a rate at least one order of magnitude higher than the average growth rate. While these measurements do not confirm a periodically interrupted shear mechanism growing at rates markedly exceeding that permitted by diffusive control, the data are limited and further study appears to be warranted.

The question of the continuity of the growth process is independent of the growth mechanism. As suggested frequently^{13,28,33} bainite can be viewed as a displacive transformation in which growth takes place at the rate permitted by carbon diffusion in austenite. Thus, the results on lengthening rates are consistent with either a ledge or a shear mechanism.

In summary, the slow growth of bainite appears to be consistent with either a displacive or a ledge mechanism for growth of bainite. However, the documented shear associated with lower bainite strongly favors the displacive mechanism and whether the rate is controlled by carbon diffusion or other relaxation processes such as accommodation strains deserves further study.

H. I. A. and K. R. K. (Round 2)

We shall first comment on four specific issues raised by Prof. Hehemann.

1) He states that the crystallography and the surface relief effect are essentially the same in low carbon martensite and in upper bainite. Although the habit plane of both lies not far from $\{111\}_{\gamma}$, that of lowcarbon martensite falls close to the $\{111\}_{\gamma} - \{001\}_{\gamma}$ circle,^{89,90} whereas that of upper bainite is definitely in the interior of the stereographic triangle and centered nearer to the $\{111\}_{\gamma} - \{110\}_{\gamma}$ circle.⁸⁶ We are not aware that the surface relief effect associated with a single ferrite plate within a sheaf of upper bainite has as yet been characterized. Single plates of proeutectoid ferrite³² and of lower bainite³³ have been found to produce the nonmartensitic relief morphology of "tents" or "vees"; it would not be surprising if individual ferrite within upper bainite do the same. Fig. 4 proves both by the constancy of thermionic emission contrast and by the absence of a ferrite:ferrite boundary, after nital etching, that the "vee" relief is produced by a single ferrite plate, rather than by a backto-back pair of plates.

2) "A significant shear strain involved in the transformation", as evidenced solely by the surface relief effect, does not prove that the atomic mechanism of the transformation is one of shear. Thus, the surface relief effect associated with the formation of hcp γ plates in fcc α Al-Ag indicates the presence of such a strain,⁹¹ but the atomic mechanism of the transformation has been established by direct observation and straightforward calculation as one of diffusional jumps of silver atoms toward and of aluminum atoms away



0.1mm

Fig. 4—Surface relief accompanying growth of Widmanstatten ferrite plate at 740°C in an Fe-0.22 pct C alloy. Portions of a thermionic emission electron microscope ciné film illustrate (a) the plate at an early stage of development and (b) at the point just prior to the refrigerated helium quench. The tent relief is clearly apparent on the etched as-quenched surface in (c) and in the interferogram in (d). The view of the polished and etched surface in (e) confirms that the entire relief effect is associated with a single crystal plate.

from the edges of ledges on the broad faces of these plates. 92

3) Concerning the question of continuity between Widmanstatten proeutectoid ferrite and upper bainite, if the former is described as isolated plates and the latter as sheaves of plates,⁴⁹ then the two reactions are not continuous by definition.* If comparisons are

*In the context of the microstructural definition, proeutectoid ferrite and bainite are completely continuous: with decreasing temperature, carbide precipitation occurs in association with a continuously increasing proportion of α plates. made between proeutectoid ferrite plates and individual plates within sheaves, on the other hand, continuity may well obtain. The results of our kinetic measurements, reported in Round 1 of this Topic, do suggest that the kinetics of lengthening and thickening, and thus the growth mechanism, may be continuous with those of proeutectoid ferrite plates. Much more extensive data are needed, of course, in order to test adequately this suggestion.

4) With respect to the questions raised as to the ability of nucleation and diffusional growth mechanisms to explain the cessation of the thickening of sheaves within the stasis region of alloy steels and the rapid increase in the rate of sympathetic nucleation in such steels at (apparently) lower temperatures, both may be answered in terms of the solute drag effect.^{20,21} The former is explained as a result of the increasingly effective inhibition of ledge growth by the solute drag mechanism as the carbon content of the adjacent untransformed austenite is increased, leading to stasis when growth has been slowed to the point where a substitutional alloying element begins to diffuse.²¹ The latter is likely due to the diminished influence which the solute drag effect appears to exert upon the kinetics of both nucleation and growth at lower temperatures.²¹

Returning now to the shear strain question, but from another point of view, if bainite plates really do grow by a shear mechanism, then the problem of providing

the free energy needed to compensate for the accompanying elastic shear strain energy must be resolved. Ko and Cottrell⁷ proposed that removal of carbon from the initially supersaturated ferrite reduces the shear strain energy required. Speich³³ points out, however, that this would result only in a volume contraction, and would not relieve the much more important shear strains. Smith, Speich, and Cohen⁹³ have shown that bainite plates grow slowly just above M_s in an Fe-1.16 pct C alloy; judging from TTT-curve data,⁹⁴ similar behavior surely prevails below. The difference in the rates of lengthening of bainite and of martensite just below the M_s temperature of this alloy is probably ca eleven orders of magnitude.^{13,95} Thus, even when the volume free energy change is sufficient to compensate for the absence of a composition change (if such be the case-which we do not believe, as will be discussed under Topic III), plus the elastic shear strain energy and any other nonchemical contribution to the temperature difference between T_0 and M_s ,⁹⁶ the growth behavior of bainite is consistent with a diffusional, rather than a shear mechanism. Terming bainite the kinetic counterpart of slowly-growing isothermal martensite is simply following another path to failure to explain the formation of bainite by shear at temperatures above M_s (or at least M_d). One must thus conclude that elastic shear strain energy, which plays such an important role in the martensite transformation, is not significantly involved in the growth of bainite and thus that such growth does not proceed by a shear mechanism.

We would finally note that even if the crystallography and the surface relief of a diffusional transformation are identical to those of a shear transformation occurring under the same conditions of crystal structures and lattice parameters, this means only that the geometry of the two transformations is probably the same. The atomic mechanisms of these transformations are entirely different. The particularly simple example of γ Al-Ag plate precipitation previously noted and the geometrically-identical martensite transformation in pure cobalt⁹⁷ provide an illustration of this statement. It is hoped that further demonstrations of the incompleteness of crystallography and surface relief as definitive evidence of reaction mechanism will soon become available in crystallographically more complex transformations.

TOPIC III: THE SOURCES OF BAINITIC CARBIDE PRECIPITATION

R. F. H. (Round 1)

In steels, it is clearly established that carbides precipitate from both austenite and ferrite during the formation of bainite.^{5,72,98} It also is well-established that carbon enrichment of austenite accompanies the formation of bainite.⁹⁹⁻¹⁰¹ However, when in the reaction sequence the enrichment occurs or the carbides precipitate is not yet firmly established. Further understanding of the transition from upper to lower bainite appears to be essential to resolving the reaction mechanism.

These two forms of bainite generally have been characterized in the following way:

1) Upper bainite consists of ferrite laths with cementite precipitated primarily at lath boundaries and there-



Fig. 5-Effect of carbon content on the transition temperature from upper to lower bainite according to Pickering.⁷²



Fig. 6—Schematic Fe-C phase diagram illustrating the proposed metastable equilibria involving ϵ carbide.

fore parallel to the growth direction. It is accepted that cementite has precipitated from enriched austenite trapped between the laths.

2) Lower bainite involves cementite located within ferrite and oriented at an angle to the growth direction of the bainite plate. ϵ carbide also has been reported in lower bainite^{69,102,103} and the ability to detect ϵ is increased by silicon additions to the steel. It has generally been assumed that these carbides have precipitated from supersaturated ferrite but the possibility that the supersaturation does not exceed that permitted by the $\alpha/\alpha + \gamma$ boundary is not yet resolved.

The influence of carbon content on the temperature for the transition from upper to lower bainite is a matter of dispute. Although I feel that this temperature is approximately 350° C regardless of carbon content of the steel, others⁷² report the dependence illustrated in Fig. 5. In this work, the transition temperature has been specified as the highest temperature at which cementite has precipitated within ferrite—presumably from supersaturated ferrite.

It has been proposed that much of this confusion arises because one or more transient intermediate states exist which have a short lifetime.^{49,69} Precipitation of ϵ carbide is the most important of these and it is the high rate at which ϵ is replaced by cementite in



Fig. 7—Lower bainite in 4340 steel, in (*a*) as formed following austenitization at 1000°C, isothermal transformation at 307°C, and a water quench. The tempered structure shown in (*b*) is the result of austenitization at 1000°C, isothermal transformation at 307° C, followed by 1 hr at 565°C and then a water quench. Nital etch; the bar represents 0.1 mm.

most steels that complicates experimental study. Thus, the relevant reactions can be studied best in silicon steels since silicon retards the precipitation of cementite severely without influencing the formation of ϵ carbide significantly.

The transformation behavior of silicon steels has led to the conclusion that there is a $\gamma - \alpha - \epsilon$ carbide equilibrium at 350°C which is responsible for the transition from upper to lower bainite.⁵³ A schematic equilibrium diagram is presented in Fig. 6 where the low-carbon region has been distorted to show the several solvus lines. In the absence of silicon to retard cementite formation, the lifetime of the metastable states involving ϵ is so short that they pass unnoticed and the structures are compatible with the γ - α diagram.

Retrogression experiments have been conducted on lower bainite in two steels—one (300M) with 1.5 pct Si and the other (4340) with about 0.3 pct Si—to help substantiate these concepts.¹⁰⁴ In both steels, 10 to 20 pct bainite was formed at 307°C and immediately tempered at 565°C (above B_s) before quenching to room temperature. Thus, the previously formed bainite is being tempered in the presence of austenite and the tempering temperature was chosen on the basis of previous ex-



Fig. 8—Lower bainite in 300M steel, in (a) as formed following austenitization at 1000°C, isothermal transformation at 307°C, and a water quench. The tempered structure shown in (b) is the result of austenitization at 1000°C, isothermal transformation at 307°C, followed by 1 hr at 565°C and then a water quench. Nital etch; the bar represents 0.1 mm.

periments which have demonstrated that bainite will not continue to grow when the temperature is raised above B_s .⁵¹

The structure of the as-formed bainite in 4340 consists of ferrite plus cementite; whereas that in 300M consists of ferrite and ϵ carbide. Tempering of 4340 produces no change in structure aside from some coarsening of the cementite. For 300M, on the other hand, the ferrite- ϵ carbide aggregate is converted to essentially carbide-free ferrite. That is, ϵ redissolves as the carbon partitions to the surrounding austenite. Typical micrographs illustrating these results are presented in Figs. 7 and 8.

The results of these experiments can be understood in terms of Fig. 6. The two structures, and carbon concentrations in ferrite and austenite, are shown schematically in Fig. 9. For 4340, the α -Fe₃C mixture is stable relative to α - γ as reflected in the inverse gradient of carbon through the ferrite. Thus, as shown in Fig. 7(b), cementite will not redissolve.

For 300M, on the other hand, the $\alpha - \epsilon$ aggregate is metastable relative to an $\alpha - \gamma$ aggregate and ϵ redissolves as carbon partitions to austenite. As shown in Fig. 8(*b*) this yields carbide-free ferrite without de-



Distance

Fig. 9-Schematic representation (not to scale) of microstructures and relevant carbon distributions during tempering at 565° C.

tectable growth of the ferrite phase.

The results of these experiments indicate that it is extremely difficult to decide on the reaction sequence by examining the carbon content of ferrite, retained austenite, or whether or not carbides are present in the structure. Specifically, bainite could initially form with supersaturation well above that permitted by the $\alpha/\alpha + \gamma$ line and yet yield microstructures varying from carbide-free ferrite to that of lower bainite depending on the relative rates of precipitation from ferrite and austenite and partition of carbon between these phases.

It is assumed that bainite forms with substantial supersaturation at all temperatures and carbon begins immediately to partition to austenite.* Below $350^{\circ}C \in$

*This assumption clearly conflicts with growth at carbon diffusion-controlled rates. Conclusions from the $\gamma \rightleftharpoons \alpha + \epsilon$ carbide equilibrium relevant to diffusion-controlled mechanisms will be considered in Round 2.

carbide precipitates very rapidly and, as indicated in Fig. 6, the α - ϵ carbide is stable relative to α - γ . This terminates the partition process. The resulting structure is lower bainite and the reduction in carbon enrichment of γ associated with lower bainite as compared to upper bainite has been demonstrated.^{69,99} In nonsilicon steels, cementite rapidly replaces ϵ in a fashion analogous to that involved in the tempering of martensite.

Above 350°C, the initial stages of the reaction are the same as before. In this case, however, the α - ϵ carbide aggregate is metastable relative to an α - γ aggregate. Thus, carbon will continue to partition until cementite precipitates from ferrite. In nonsilicon steels, cementite precipitates relatively rapidly from ferrite which restricts somewhat the amount of enrichment observed and these precipitates also would be responsible for the difference in opinion regarding the temperature for the transition from upper to lower bainite shown in Fig. 5. Eventually additional cementite precipitates from the enriched γ so that upper bainites formed near 400°C exhibit carbides precipitated from both α and γ .^{5,49,72}

Silicon in the steel so retards precipitation of cementite that upper bainite is free of carbide at all temperatures above $350^{\circ}C$.⁶⁹

According to these concepts the critical step that defines the formation of both upper and lower bainite is the formation of ferrite with substantial supersaturation by a shear transformation. The degree of supersaturation may be less than the average carbon content of the steel but is well above that of the $\alpha/\alpha + \gamma$ line. Both upper and lower bainite are considered to form by the same mechanism and their differences arise from the relative rates (and stabilities) of the several reactions involved in the transformation. Nevertheless, it is of value to retain the established distinction between them since the differences in carbide distribution result in significantly different mechanical properties for upper and lower bainite.

H.I.A. and K.R.K. (Round 1)

On the basis of room temperature microscopy, one can be fairly (though not entirely) certain that a particular carbide precipitated from austenite at an austenite:ferrite boundary only when that carbide lies almost wholly within the austenite phase (martensite at room temperature). Room temperature microscopy can provide statistical evidence that a substantial proportion of the bainitic carbides precipitated from ferrite only when the average density of carbides within areas which have been transformed wholly to ferrite increases substantially at later reaction times. Evidence of the former type is reasonably accessible, particularly at high reaction temperatures,^{105,106} but can account with certainty for only a small proportion of the bainitic carbides in a given microstructure. Although some evidence of the latter type has been reported,¹⁰⁶⁻¹⁰⁹ this is very rare simply because the time interval between ferrite and carbide precipitation is usually shorter than the smallest practicable interval between treatments. In principle, the combination of hot-stage transmission electron microscopy and cinematography has sufficient resolution in both time and space to account for the origin of each bainitic carbide formed within a given field of view over a wide (and perhaps the entire) range of reaction temperatures of interest-provided that the microscope atmosphere and/or the thinness of the foil do not significantly compromise the mechanism of the transformation. However, an investigation of this type has yet to be reported. Crystallographic studies of the orientation relationships between bainitic carbides and ferrite and between such carbides and austenite have suggested that these carbides precipitate from austenite in upper bainite and from ferrite in lower bainite.^{5,110} Although ingenious, these studies are indirect; their results are consistent with microscopy at high temperature and are thus probably correct; in the lower bainite region, on the other hand, results to be presented here lead to a quite different conclusion as to the primary source of bainitic carbide precipitation.

In view of the foregoing difficulties, this Topic is customarily attacked from a level once removed from that of carbide precipitation, namely the (initial) carbon content of the ferritic component of bainite (FCB). Although a "layer" of nucleation and growth kinetics intervenes between this composition and the actual carbide precipitation processes, at least at the limiting values of the carbon content reliable deductions can be made as to the phase from which the carbides will precipitate. If the ferrite inherits essentially the entire carbon content of the parent austenite, precipitation almost exclusively from ferrite seems inevitable. Conversely, if the carbon content of the ferrite lies at or below that of the extrapolated $\alpha/(\alpha + \gamma)$ curve, a large proportion (though not all) of the carbide must precipitate from the austenite.

Although many attempts have been made to deduce the carbon content of the FCB from physical and chemical measurements such as dilatometry, ^{111,112} calorimetry, ¹¹² chemical extraction, ¹¹³ and resistometry, ^{113,114} the precipitation of ϵ carbide has made the interpretation of these measurements uncertain. ^{112,114} Deliry¹⁰³ has made a more detailed dilatometric study of the bainite reaction in silicon steels and concluded that the FCB in these steels has effectively the carbon content of the original austenite at temperatures near M_s . However, his assumption that ϵ carbide precipitates only from ferrite, though often made, is unverified* and his

*Why cannot ϵ precipitate from austenite at austenite:ferrite boundaries? use of the contraction of martensite during ϵ formation as a reference value for the bainite measurements adds a further measure of uncertainty. Most X-ray data, on the other hand, indicate no detectable (<0.1 pct) C in the FCB.¹¹⁵⁻¹¹⁷ Those results which yield a contrary conclusion are based upon detection of a c/a ratio for ferrite greater than unity,^{69,118} and may have been caused by the formation of bainite-stimulated martensite at temperatures below M_d^{93} which was then partially autotempered. In effectively all cases, however, the X-ray studies had to be made at late stages of reaction in order to minimize interference from martensite, and are thus not necessarily a good measure of the carbon content of the FCB during the more important early stages of transformation.

Recently, electron probe analysis has been used to demonstrate conclusively that during the early stages of reaction at temperatures below the kinetic- B_s both kinetically defined and surface relief bainite have carbon contents less than the detectability limit (0.03 pct) of the probe in Fe-0.11 pct C-1.95 pct Mo and Fe-0.13 pct C-2.99 pct Cr alloys.¹¹⁹ A large proportion of the bainitic carbides which formed in these microstructures must thus have precipitated from the austenite.¹²⁰

We shall conclude by presenting a brief summary of a new method for deducing the carbon content of the FCB.¹²¹ This method is of especial interest at lower reaction temperatures and higher carbon contents, where the minimum dimension of areas containing only ferrite is usually less than 2μ and useful electron probe measurements are thus infeasible. The method is based upon the observation that in hypoeutectoid steels, particularly those appreciably alloyed with silicon or aluminum, retained austenite containing a substantially higher average concentration of carbon than the alloy as a whole is often associated with partial transformation to bainite.^{99,101,122-124} The principal assumptions made in the first step of this analysis are



Fig. 10—Schematic representation of the carbon-enriched austenite region associated with one broad face of a ferrite plate.



Fig. 11--Variation of $\vec{x'_{j}}$ with reaction temperature as calculated (dashed lines)^{84,128} and as experimentally determined (solid lines) by L. M. Pevzner *et al.*¹²⁹

the following: a) austenite:ferrite boundaries are planar (accurately fulfilled experimentally in most instances); b) bainitic carbides had not precipitated from austenite at the time the X-ray measurements of the carbon content of the retained austenite were made (evidently correct in silicon and aluminum steels^{13,109}); c) the carbon diffusion fields of adjacent ferrite plates do not overlap (not fulfilled, but found numerically not to introduce a significant error); d) thickening of ferrite plates is controlled by the diffusion of carbon in austenite (this definitely wrong assumption^{32,61} is the price paid for mathematical tractability; a correction is made for it, however, in the second step of the treatment); and e) the proportional volume of the austenite regions not affected by the carbon diffusion fields of ferrite plates is negligible (probably a reasonable assumption when the experimentally-determined value of the average mole fraction of carbon in the retained austenite, $\overline{x'_{\gamma}}$, reaches its maximum value). The shaded

area in the sketch of Fig. 10 represents the carbonenriched austenite region associated with one broad face of a ferrite plate. Calculation of $\overline{x'_{\gamma}}$ is complicated by the fact that a proportion of this region, which varies with carbon content, transforms to martensite during quenching and is thus excluded from the lattice parameter measurement through which the average carbon content of the retained austenite is determined. In schematic form, the equation for $\overline{x'_{\gamma}}$ is:

$$\overline{x}'_{\gamma} = \frac{\int\limits_{s_i}^{s_c} f\{s, x\} x\{s\} ds}{\int\limits_{s_i}^{s_c} f\{s\} ds}$$
[1]

where $x\{s\}$ = mole fraction of carbon in austenite as a function of the perpendicular distance, s, from a planar $\gamma:\alpha$ boundary, $^{125,126}_{125,126}f\{s, x\}$ = fraction of austenite re-tained as a function of x, and thus of s, $^{127}_{125,126}s_i$ = position of the $\gamma: \alpha$ boundary at a given growth time and $s_c = po$ sition in the austenite beyond which carbon-enrichment can be considered negligible. Integration of the numerator required that $f\{s, x\}$ be expressed as a series of five linear equations; in combination with the error function-containing expression for $x\{s\}$, this leads to a very cumbersome equation. The dashed line in Fig. 11 shows the variation of $\overline{x'_{\gamma}}$ with reaction temperature calculated for an aluminum and a silicon steel. (Phase boundary concentrations were adjusted for the presence of alloying element on the basis of no partition of this element between austenite and ferrite.^{\$4,128}) The solid lines in this figure are taken from the experimental results of Pevzner et al.¹²⁹ for these steels. Ascribing the divergence of these curves to the increasingly effective barrier to growth at the broad faces of ferrite plates with decreasing temperature.^{38,61} the second step in this analysis consists of a trial-and-error calculation of the reduction in the carbon content of the austenite at the austenite;ferrite boundary required to bring the two curves into coincidence as a function of temperature. An "effective Ae3" curve is thereby produced. This calculation assumes, solely for the reason of mathematical feasibility, that the barrier to growth is of the "uniform braking" type rather than a nearly coherent interfacial structure¹³⁰ which is partially circumvented by means of the ledge mechanism. Noting that carbon should be able to diffuse freely through this interfacial structure, the partial molar free energy of the carbon in austenite at the composition of the "effective Ae3" is equated to that in ferrite, again as adjusted for the presence of alloying element. On this basis, the carbon content of the FCB is computed vs temperature, with results as shown in Fig. 12. This carbon content is seen to lie between those of the $\alpha/(\alpha + Fe_3C)$ and the extrapolated $\alpha/(\alpha + \gamma)$ phase boundaries. Although use of the uniform barrier model limits the accuracy of the calculated carbon contents, they are nonetheless in accord with qualitative expectation from the barrier concept. This result, which is applicable to any bainite in steel whose ferritic component has the Widmanstatten morphology, indicates that much the largest proportion of carbides must precipitate from austenite (presumably at austenite:ferrite boundaries) in the lower as well as in the upper bainite region.



Fig. 12—The computed carbon content of the ferritic component of bainite vs reaction temperature.



Fig. 13—Austenite retention during the course of the bainite reaction.

R. F. H. (Round 2)

While it is firmly established that much of the carbide in upper bainite precipitates from austenite, this need not exclude the possibility that bainite formed initially with supersaturation as has been noted in Round 1 on this Topic. In particular, theoretical considerations¹³¹ indicate that the time for complete decarburization of an initially supersaturated ferrite lath is substantially less than 1 sec. Thus, the microprobe measurements¹¹⁹ of the carbon content in the ferritic component of upper bainite (<0.03 pct) do not provide conclusive evidence that the ferrite formed without supersaturation. The same reservation applies to the X-ray measurements reported by Drs. Kinsman and Aaronson since these rely on an evaluation of the activity of carbon in ferrite from that of austenite (assuming no carbide precipitation from austenite) with which it is equilibrated at a relatively late stage of the reaction. Thus, the analysis automatically assumes that all carbon inherited by the ferrite during growth is held there and not subsequently partitioned to the surrounding austenite. This need not be valid as demonstrated by the retrogression experiments presented in Round 1.

The maximum temperature (350°C) at which ϵ carbide occurs in bainite formed in silicon steels^{69,103} corresponds to that for the maximum carbon content of retained austenite as reported in Fig. 11. This precipitation (which invalidates their assumption (b) unless these carbides precipitated from supersaturated ferrite) rather than a temperature dependent barrier to thickening may be responsible for the maximum. As illustrated in Fig. 13, the propensity for austenite retention also changes drastically in this temperature range, thereby suggesting much less extensive carbon enrichment. In these silicon steels, all of the carbon in the steel is contained in the retained γ for reaction temperatures above 350°C; whereas, a substantial fraction of the carbon is present as ϵ carbide when bainite is formed below 350°C.^{68,69,103} It appears that alternate explanations⁶⁸ to the barrier concept for the discrepancy between the observed carbon content of the enriched γ and that expected from the $\alpha/\alpha + \gamma$ equilibrium line warrant further consideration.

The assumption that ϵ carbide cannot precipitate from austenite is inherent in the view that lower bainite follows a reaction sequence analogous to that in the tempering of martensite. Drs. Kinsman and Aaronson rightfully challenge this assumption. The $\gamma \rightleftharpoons \alpha + \epsilon$ carbide equilibrium permits lower bainite to form, in principal, as a eutectoid reaction.^{53*} The subsequent

*The high carbon content of the eutectoid composition (3 to 4 pct) provides a possible explanation for the absence of proeutectoid ϵ carbide precipitation from austenite.

replacement of ϵ carbide in this aggregate by cementite would occur within the ferritic matrix. Thus, the crystallographic evidence^{5,72,110} for precipitation of cementite from ferrite is probably valid but need not provide a clue to the reaction mechanism. The growth of upper bainite at the rate permitted by carbon diffusion, as reported by Drs. Kinsman and Aaronson, favors models based on local equilibrium during growth but the data here are limited and the growth rate required to sustain supersaturation is not yet known.

Several features of these reactions require further clarification in terms of separate precipitation of ferrite and carbide from austenite. For example the explanation offered in Round 1 of this Topic for the transition from upper to lower bainite must be discarded. Of greater importance, however, is the question of why there should be any detectable transition in the nonsilicon steels on which the crystallographic studies have been conducted. In addition, lower bainite plates exhibit a single uniform relief but have carbides precipitated rather uniformly within them at interparticle spacings comparable to those in tempered martensite. It is not clear why any relief, let alone one with a welldefined shear component, should be observed if the structure develops by precipitation of both ferrite and carbide from austenite.

H. I. A. and K. R. K. (Round 2)

The experiments on the retrogression or reversion of ϵ carbide reported by Prof. Hehemann in Round 1 on this Topic are most interesting. Systematic pursuit of this line of research, say on high-purity Fe-C-Si alloys, may enable a decision to be reached as to whether or not the metastable equilibrium in which the ϵ phase participates involve a eutectoid reaction. The metastable equilibrium configuration at low-carbon contents and its relationship to the extrapolated $\alpha/(\alpha + \gamma)$ phase boundary are of particular importance.

Prof. Hehemann assumes that the ferritic component of bainite initially contains substantially more carbon than that corresponding to the extrapolated $\alpha/(\alpha + \gamma)$ boundary. This assumption is, of course, quite commonly made. In our presentations on both this and the preceding topic, however, we have challenged this assumption on both experimental and calculational grounds. Although disproof of this key assumption is perhaps not yet complete, we would hope that the failure of the assumption to meet the challenges so far offered may prove sufficiently worrisome to inhibit somewhat the tendency to build still further upon this rather insecure foundation. The finding, reported in Round 1 of Topic II, that individual plates in upper bainite sheaves grow at or more slowly than the rates allowed by the volume diffusion of carbon in austenite, should be particularly important in this reconsideration. As Prof. Hehemann himself has $recognized^{53}$ and as did J. C. Fisher¹³² earlier, the 100-fold higher diffusivity of carbon in ferrite than in austenite must preclude extensive supersaturation of ferrite with respect to carbon when the austenite-ferrite boundary is displaced with those kinetics.

SUMMARY

R. F. H.

TOPIC I-WHAT IS BAINITE?

Until the mechanism of the bainite reaction is more firmly established, it seems advisable to define bainite in terms of the principal experimental characteristics from which the mechanisms must be deduced. The most useful characteristics are:

1) In steels, bainite is a nonlamellar ferrite-carbide aggregate, but several variants are recognized.

2) The transformation product exhibits relief and develops at a slow rate.

3) In alloy steels, a clearly-defined temperature exists, B_s , above which austenite will not transform to bainite and a temperature dependent, incomplete reaction is observed below B_s . Experimental difficulties

from overlapping reactions have prevented agreement on the generalization of these observations to plain carbon steels.

These features of the reaction are discussed in terms of diffusion-controlled and diffusionless transformation mechanisms.

TOPIC II—THE GROWTH MECHANISM OF THE FERRITIC COMPONENT OF BAINITE

The demonstration by Srinivasan and Wayman that lower bainite forms by shear is accepted as the basis for considering the austenite-ferrite interface to be of the same character as that in martensite transformations. The similarity in substructure between upper bainite and low carbon martensite suggests that this conclusion can be extended to upper bainite in spite of the lack of experimental evidence for this case.

The factors that control interface propagation are less clearly understood. Experimental growth rates agree exceptionally well with those calculated from a model-based on diffusion of carbon in austenite. However, the principal experimental question is whether growth occurs continuously or discontinuously as the result of a repeated nucleation and growth process. In the latter case, diffusionless growth can occur at a rate determined by an appropriate relaxation process.

TOPIC III-THE SOURCES OF BAINITIC CARBIDE PRECIPITATION

The reason for the transition from upper to lower bainite is explored in a silicon-modified 4340 steel. In silicon steels, upper bainite forms at temperatures above 350°C and consists of essentially carbide-free ferrite; whereas, lower bainite forms at temperatures below 350°C and consists of a ferrite-€ carbide aggregate. The temperature for this transition in silicon steels corresponds to that in nonsilicon steels over a wide range of carbon contents. These results suggest that an invariant metastable $\gamma \rightleftharpoons \alpha + \epsilon$ carbide equilibrium exists at this temperature. Reversion experiments provide some support for this concept and demonstrate that ϵ carbide in lower bainite can be redissolved and carbon partitioned to austenite by tempering at a temperature above 350°C. These results indicate that lower bainite could form from austenite as an $\alpha - \epsilon$ carbide aggregate. This removes the need for, but does not disprove, the assumption that bainite forms initially with supersaturation.

H. I. A. and K. R. K.

TOPIC I-WHAT IS BAINITE?

Three clearly different definitions of bainite have been shown to be currently in use.² These definitions and the disposition recommended for each are the following.

1) The microstructural definition, in its generalized form, describes bainite as the product of a *nonlamellar* eutectoid reaction. No restriction is placed, however, upon the morphology of the ferritic component. On this view, bainite is the counterpart of pearlite, the product of a *lamellar* eutectoid reaction. For both, the presence of carbides is essential, and the eutectoid temperature serves as the maximum temperature at which they can form. On the grounds of both historic precedence^{1,17} and mechanistic generality and importance, the generalized microstructural definition is recommended for adoption as *the* definition of bainite.

2) The kinetic definition is based upon overall reaction kinetics:¹⁹ bainite has a separate C-curve for the initiation of transformation whose upper limit, the kinetic- B_s , lies well below the eutectoid temperature; when no other reaction intervenes, the fraction of the austenite which can be transformed to bainite approaches zero as the reaction temperature approaches that of the kinetic- B_s . TTT-diagrams of this type have been found, however, to be intimately related to the growth kinetics of proeutectoid ferrite.^{20,21} These kinetics (which are probably an experimentally more readily detectable indication of such TTT-diagram behavior than the diagram itself), exhibit a minimum at the kinetic- B_s only when an alloying element which appreciably decreases the activity of carbon in austenite is present in sufficient concentration.^{20,21} Incompleteness of transformation has also been found to be an alloying element effect.²¹ The kinetic definition of bainite is thus unsuitable on the ground of insufficient generality.

3) The surface relief definition 7,22 describes as bainite any slowly growing precipitate plate which vields a martensitic surface relief effect. Relief effects associated with single plates of proeutectoid ferrite,³² which are considered bainite by Ko,²² and with single plates of lower bainite,³³ however, often have a veeshape rather than the single planar tilt morphology characteristic of martensite. Evidence for solute partition between matrix and precipitate in the case of α brass plates,³⁵ which evidently do develop martensitic relief effects and crystallography but which cannot exhibit partition during growth if the mechanism is one of shear because both matrix and precipitate in this case are substitutional solid solutions,²⁸ provides further evidence of the fundamental unsoundness of this definition. Now representing no more than a historically inappropriate attempt to replace the long-established term "Widmanstatten structure", this definition should be discarded.

TOPIC II-THE GROWTH MECHANISM OF THE FERRITIC COMPONENT OF BAINITE

In order to match the considerations of Prof. Hehemann, this discussion was confined to the Widmanstatten morphologies of the ferritic component of bainite.

1) In high-purity Fe-C alloys, the ferrite and bainite plate lengthening data of Simonen *et al.*⁷⁹ the ferrite plate thickening data of Kinsman *et al.*³² and related observations show that both processes are controlled by the formation and lateral migration of ledges. In the case of thickening, lateral migration has been found to be controlled by the diffusion of carbon in austenite.³²

2) Both parts of the proposal⁴⁹ that the individual plates in bainite sheaves grow at rates much more rapid than those allowed by the diffusion of carbon in austenite, and then cease to grow until additional sympathetic nucleation occurs, were proved incorrect through measurement and analysis of the lengthening and thickening kinetics of such plates in sheaves of upper bainite formed in alloy steels.

3) The view²⁸ that the crystallography of upper bainite is that of low-carbon martensite and that of lower bainite is the same as that of martensite formed in the same alloy is widely accepted. However, the habit plane of upper bainite is different from that of lowcarbon martensite^{89,90} and cannot be understood on the basis of the phenomenological theory of martensite.³⁶ The habit plane of lower bainite differs markedly from that of martensite in the same alloy.^{11,87} Accounting for the lower bainite habit plane in terms of martensite crystallography requires acceptance of the postulate that a physically unreasonable contraction of the ferrite lattice occurs during transformation.¹¹

4) On an argument by Speich,³³ the problem of reducing the elastic shear strain energy sufficiently to allow a shear transformation to take place above M_s (in the absence of a composition change) has not been solved by Ko and Cottrell⁷ or by subsequent workers.

5) Taken together, these considerations and the surface relief observations noted under Topic I lead to the conclusion that shear plays no role whatsoever in the growth mechanism of the ferritic component of bainite.

TOPIC III—THE SOURCES OF BAINITIC CARBIDE PRECIPITATION

1) The direct evidence on the relative importance of bainitic carbide precipitation from ferrite vis-a-vis that from austenite at austenite:ferrite boundaries is very limited, and most of the indirect evidence is of uncertain value.

2) The most important indirect approach to this problem has been through attempts to determine the carbon content of the ferritic component of bainite. The following studies have supplied determinations which appear to be at least qualitatively valid:

a) Measurements of bainite growth kinetics,^{9,10,45,47} whose significance is reenforced by the results which we reported in Round I of Topic II, indicate that these kinetics are too slow to support an appreciable super-saturation relative to the extrapolated $\alpha/(\alpha + \gamma)$ curve.

b) Measurements of the carbon content of ferrite allotriomorphs and plates formed during early stages of reaction below both the kinetic- and the surface relief- B_s temperatures in alloy steels containing 0.11 pct C and 0.13 pct C, respectively, by means of electron probe analysis yielded values below the detectability limit (0.03 pct C) of the instrument.¹¹⁹

c) An analysis of literature data on the average carbon content of retained austenite associated with partial transformation to bainite (summarized under Topic III) indicates that in both the upper and the lower bainite regions the carbon content of the ferritic component of bainite lies between the $\alpha/(\alpha + Fe_3C)$ and the extrapolated $\alpha/(\alpha + \gamma)$ phase boundaries.

3) From the foregoing, one must conclude that precipitation from austenite at austenite:ferrite boundaries is most likely to be the primary source of bainitic carbide precipitation. Some carbides, however, can be and probably are precipitated from ferrite.

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