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Discussion

On the influence of a solute drag-like effect upon the growth of ferrite in Fe–C–X alloys

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1. Introduction

Bhadeshia [1] has recently published a paper dealing with solute drag effects upon the proeutectoid ferrite reaction in steel. Aside from an extended summary of already well known facts and theory concerning the solute drag-effect upon the migration kinetics of grain boundaries, this paper was actually almost entirely a discussion to a series of papers by Aaronson and coworkers [2–9] in which a solute drag-like effect upon the growth kinetics of grain boundary ferrite allotriomorphs is proposed and elaborated. Bhadeshia concluded that "the experimental evidence for the existence of solute drag at transformation interfaces in steels is very doubtful". The present paper, prepared as a reply to Bhadeshia's discussion, will demonstrate that this conclusion did not take full account of the experimental evidence published in this series of papers. Other discrepancies in his arguments will also be noted.

2. Omissions of published experimental evidence for the solute drag-like effect

Bhadeshia utilized only the experimental data on the thickening kinetics of grain boundary ferrite allotriomorphs in an Fe–0.11% C–1.95% Mo alloy reported by Kinsman and Aaronson [2]. These data extended from 875 down to 720° C, the latter temperature lying about half-way between the upper nose in the TTT-curve for the beginning of transformation and the bay in this curve. He omitted the data of Boswell, Kinsman and Aaronson published by Aaronson *et al.* [4] in 1970 (Bhadeshia's reference [30]) on the same alloy which extended down to 550° C, a temperature located well below the bay in the TTT-curve for the initiation of transformation in this alloy. He also omitted the fully reported data of Bradley and Aaronson [5], published in 1981 (Bhadeshia's reference [31]), in which thickening kinetics significantly slower than those derived on the assumption of para-equilibrium transformation were clearly demonstrated for Fe–0.12% C–3.08% Mn and Fe–0.13% C–2.99% Cr alloys. The Boswell *et al.* data on the parabolic rate constant, α, for allotriomorph thickening kinetics were compared [4] with the rate constant calculated from the Dube [10]– Zener [11] equation for a planar, disordered austenite–ferrite boundary. The calculated rate constant was found to pass through a maximum at almost exactly the same temperature, 625° C, at which the experimental rate constant went through a well defined minimum. The calculated constant is about 1.5 orders of magnitude higher than the experimental one. This difference was foreshadowed in the earlier data of Kinsman and Aaronson [2] but was now experimentally demonstrated.

Bhadeshia also incorrectly described the rate

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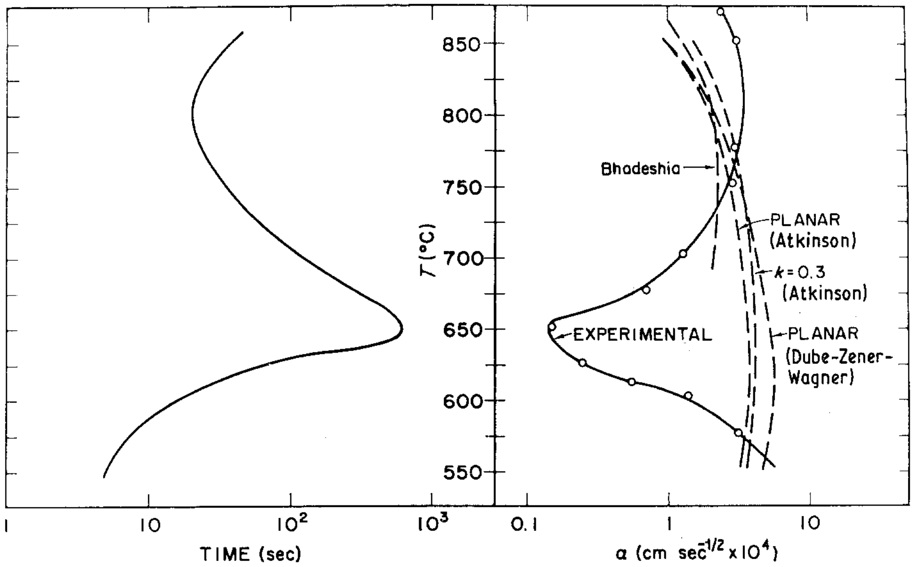

Figure 1 (a) TTT-curve for initiation of transformation in an Fe–0.11% C–1.95% Mo alloy [39]. (b) Experimental values of the parabolic rate constant for the thickening kinetics of grain boundary ferrite allotriomorphs in this alloy (which contain various dispersions of carbides at lower temperatures) [39]. Calculated values of the constant against temperature are secured on the various bases described in the text.

constant calculation made by Kinsman and Aaronson. He claimed that they failed to "allow for the concentration dependence of the diffusivity of carbon in austenite". However, they did do so, using what was then the "state of the art" approach, namely, the Wagner [12] approximation, wherein the diffusivity used is that corresponding to the carbon concentration in austenite in contact with the austenite–ferrite boundary, $x_\gamma^{\gamma\alpha}$. He also stated that their calculated rate constant (which he termed α_1) "indicated a monotonically increasing α_1 with decreasing temperature". However, this result derived from extension of their calculations only to the lowest temperature at which they were able to acquire experimental data. An indefinitely increasing rate constant is, of course, a physical impossibility because of the diminution in the diffusivity of carbon in austenite with decreasing temperature, and could not have been obtained from the equation used by Kinsman and Aaronson.

Fig. 1 shows the TTT-curve for the beginning of transformation, and replotted α against temperature data of Boswell *et al.* for the thickening kinetics of ferrite allotriomorphs compared with the calculated plots presented by Boswell *et al.* and by Bhadeshia and recomputed for this Discussion with the present "state of the art" analysis. The latter is the Atkinson [13, 14] treatment of the growth kinetics of an oblate ellipsoid. In this analysis, the influence of the variation of the diffusivity of carbon in austenite with carbon concentration is taken fully into account with a computerized analytical technique. The Atkinson calculation was executed twice, once for an aspect ratio of 1/3, the value often found for ferrite allotriomorphs in Fe–C–X alloys [5, 15] and again for an aspect ratio of zero, i.e., the planar boundary case. Differences among the four calculated curves are seen in Fig. 1 to be quite small (except for the Bhadeshia plot, at lower temperatures). In the bay region, the Boswell *et al.* and the two Atkinson-type plots fall well above the experimental α against temperature curve. Fig. 1 now represents the strongest published evidence in support of a solute drag-like effect presently available. Shiflet and Aaronson [16] have in press a paper on transformation kinetics in Fe–C–Mo alloys in which the type of result shown in Fig. 1 is repeatedly confirmed, and is shown not to be explicable on the basis of either interphase boundary or fibrous carbide precipitation. Earlier, Shiflet *et al.* [7] demonstrated with TEM that the substantial deviations from para-equilibrium growth kinetics previously noted for an Fe–C–Mn and an Fe–C–Cr alloy [5] cannot be accounted for by carbide precipitation at austenite–ferrite boundaries simply because this precipitation did not occur within the temperature–time envelopes used for the grown kinetics measurements. These data also appear difficult to explain in any way other than through a SDLE.

3. Misunderstandings of theory of the solute drag-like effect

1. Bhadeshia writes: "Cahn's theory (his reference [13]) clearly shows, for the grain boundary case, that the solute profile in the vicinity of the moving interface always extends into the regions beyond the interface . . ."

As Kinsman and Aaronson originally noted and as has become increasingly clear since then, particularly from the recent work of Bradley and Aaronson [5], diffusion of X in austenite during growth in the time–temperature intervals in which measurements were made is negligible. Hence the term "solute drag-*like* effect" is employed; the segregation of interest is accordingly considered to take place solely *within* austenite–ferrite boundaries. Efforts have been repeatedly made to distinguish between a solute drag effect during grain growth and that proposed to accompany the growth of ferrite in some Fe–C–X systems [2–5]; Bhadeshia's objection fails to recognize this distinction.

2. Bhadeshia makes the obvious point that equilibrium segregation of X can occur only to the extent that the partial molar free energy of each species will become the same throughout the system.

The central problem in placing the SDLE on a quantitative basis is that of devising, and explicitly characterizing, a source of X segregation which will cause the activity of carbon in austenite at austenite–ferrite boundaries to deviate from that which obtains at paraequilibrium. An extensive effort to solve this problem is presently in progress [17].

3. Bhadeshia states that

"If an X element reduces the activity of carbon in austenite, then to maintain this equality of partial molar free energies, the concentration (and hence concentration gradient) of carbon (i.e., $x_\gamma^{\gamma\alpha}$) must correspondingly increase, in contradiction with Kinsman and Aaronson's hypothesis."

Equality of the partial molar free energy of carbon in austenite with that in ferrite at an austenite–ferrite boundary can be maintained by adjusting the carbon concentrations in contact with this boundary on both sides of the boundary. Reduction in the partial molar free energy of carbon in austenite at the boundary will thus be accompanied by reduction in the partial molar free energy of carbon in ferrite at this boundary. We visualize these reductions as being accomplished through the non-equilibrium segregation of an alloying element, X, which reduces the activity of carbon in austenite in both phases. Once the carbon activity corresponding to $x_\gamma^{\gamma\alpha}$ is reduced, diminution of all carbon concentrations between $x_\gamma^{\gamma\alpha}$ and x_γ (the bulk carbon concentration prior to transformation) follows directly.

4. Refutation of experimental evidence apparently opposing SDLE theory

1. Alloying elements which raise the activity of carbon in austenite are claimed to produce a bay in the TTT-diagram.

The appearance of a bay in the TTT-diagram of an Fe–C–Mn–Si alloy [18] is said to support this statement. As shown in a discussion to a paper by Bhadeshia and Edmonds [19], however, only carbon activity data in Fe–C–Si alloys are used to support this statement; no data on carbon activity in austenite in Fe–C–Mn–Si alloys were cited. Subsequently, it was stated that through the use of Wagner interaction parameters and the thermodynamics of multicomponent solid solutions the activity of carbon in austenite was shown to be higher in their alloy than in "a plain carbon steel" [19]. The ambiguity in this statement aside, the possibility nonetheless remains that the concentration of manganese at disordered areas of austenite–ferrite boundaries is increased in the presence of silicon, with a concomitant increase in the SDLE. Hehemann [8] has previously made a similar criticism and referenced the work of Sheehan *et al.* [20] on Fe–C–Ni alloys and his own studies on Si-containing steels [21]. However, inspection of the Sheehan *et al.* TTT-diagrams quickly demonstrates that the bay usually arises in these alloys because they are hypereutectoid and proeutectoid carbide forms at higher reaction temperatures whereas ferrite/bainite develops at lower temperatures. The situation to which SDLE theory has been applied, however, is one in which ferrite/bainite is the initial product of transformation *both above and below* the bay temperature. The silicon steels studied by Hehemann represent a different situation. As Liu *et al.* [18] have demonstrated in the aforementioned discussion, interaction between two substitutional alloying elements, X_1 and X_2, can give rise to the incomplete transformation and the bay phenomena during ferrite formation even though Fe–C–X_1 and Fe–C–X_2 alloys containing essentially the same proportions of C and X_1 or X_2 as the quaternary alloy do not exhibit either phenomenon.

2. On the basis of FIM-atom probe results [22], Bhadeshia claims to have established the absence of X segregation at bainitic ferrite–austenite interfaces.

This claim is readily refuted on two independent grounds. An Fe–C–Mn–Si alloy was again used. However, the authors were unable to image manganese atoms. Their claim that segregation of manganese would have shown up through effects on the distribution of the other solutes is rather unconvincing. Given the diluteness of the solutions involved and the scatter in the data, only a direct quantitative demonstration that manganese does not segregate to austenite–ferrite boundaries could have been meaningful.

The second ground is that X segregation is considered to occur at disordered areas of austenite–ferrite boundaries [2–5]. The proportion of austenite–ferrite boundaries which appears to be disordered, particularly when ferrite develops in the plate morphology, however, is rapidly shrinking as the resolving power of TEM increases and the techniques of utilizing TEM improve [23]. Unless the atom probe measurements on bainite plates had been made on those areas of the risers of growth ledges which had a disordered structure, much less, or possibly no segregation at all should have been observed. Presumably such segregation would be more readily found at the interphase boundaries of grain boundary allotriomorphs, since these should contain a higher proprotion of disordered area. However, lack of detailed knowledge of the latter interfaces would seriously hamper the interpretation of such data at the present time. A more complete discussion of Bhadeshia's atom probe studies is in preparation.

3. Bhadeshia uses the results of the investigation by Sharma *et al.* [24] on pearlite formation in Fe–C–Mn alloys to claim the absence of a SDLE during the pearlite reaction.

However, Chance and Ridley [25] interpret their data on pearlite growth kinetics in Fe–C–Cr alloys as indicating that a SDLE is present. In view of the role which interphase boundary diffusion can play in the pearlite reaction [26], it would not be surprising if the SDLE affects this reaction differently and perhaps less than that of proeutectoid ferrite.

5. Consideration of some alternate mechanisms for slow growth kinetics and bay formation

Here consideration is confined to two mechanisms noted by Bhadeshia but originally proposed by others. Critical comments on Bhadeshia's frequent urgings that all things bainitic can be explained by shear have already been made in previous discussions [18, 27, 28].

1. Carbide precipitation at austenite–ferrite boundaries is a possible source of such effects [29]. Diffusion of X is required to form interphase boundary alloy carbides; this is claimed to have been ignored by Shiflet *et al.* [7].

As already noted, Shiflet *et al.* [7] showed that in the Fe–C–Mn and Fe–C–Cr alloys in which Bradley and Aaronson [5] had found slow growth kinetics there was no carbide formation at austenite–ferrite boundaries within the temperature–time envelopes employed for measurements of growth kinetics. Shiflet and Aaronson [16] subsequently considered the role of molybdenum diffusion in the formation of Mo_2C as interphase boundary carbides and have shown that there is sufficient time between the passage of successive ledges and sufficient atomic mobility of molybdenum at the reaction temperatures used so that Mo_2C can form at stationary, partially coherent austenite–ferrite boundaries by volume diffusion of molybdenum through austenite. In an earlier study, Obara *et al.* [30] demonstrated that Mo_2C probably forms only on partially coherent austenite–ferrite boundaries in an Fe–0.11% C–1.95% Mo alloy.

2. The pearlite reaction forms the upper C-curve and the bainite reaction the lower C-curve in alloys exhibiting a bay in the TTT-diagram.

Bhadeshia references Christian [31] for this explanation; many earlier proposals of the same explanation are readily found [32]. No doubt this mechanism is useful, particularly in eutectoid steels, though even in this circumstance it can be questioned [33]. However, the situation considered by Kinsman and Aaronson [2] *et seq.* is the hypoeutectoid one in which ferrite/bainite form both above and below the bay region. Hence this mechanism is irrelevant to the present discussion.

6. Supplementary considerations

1. Bhadeshia states that Kinsman and Aaronson failed to take into account the influence of X upon the diffusivity of carbon in austenite.

Kinsman and Aaronson, having worked with an Fe–C–Mn and an Fe–C–Mo alloy, explicitly noted that neither manganese [34] nor molybdenum [35] has a significant effect upon the diffusivity of carbon in austenite, using the references again employed here. McLellan and Ferrarro [36] have treated this problem theoretically and attempted comparisons with experiment. Much of the data available on this subject were collected by Krishtal [37]; McLellan and Ferrarro were particularly critical of these data and pointed out that considerably more accurate (and reliable) information is needed before any experimentally based generalizations can be made. McLellan [38] has privately stated, however, that there is little reliable indication now available to indicate that these effects are large.

2. Bhadeshia criticizes the supposed extrapolation of measurements on allotriomorph growth kinetics into the bainite range. In the latter range, he clearly implies, allotriomorphs cannot be present because bainite forms by shear whereas allotriomorphs do not.

This criticism is inappropriate, as it bears little resemblance either to the relevant literature or the experimental facts. Except in the paper by Kinsman and Aaronson which introduced the SDLE, extrapolation was not employed. Note that the experimental data of Fig. 1 on an Fe–C–Mo alloy extend *below* the bay (and justify the extrapolation made earlier by Kinsman and Aaronson) (KA), and that the data of Bradley and Aaronson on Fe–C–Cr extend into the bay region.

Bhadeshia's views on the connection between shear and the overall reaction kinetics definition of bainite [3] to the contrary, grain boundary allotriomorphs can become the only morphology of ferrite/bainite in the bay region of Fe–C–X alloys containing sufficiently high proportions of chromium or molybdenum [3, 16, 39]. All of the post-KA evidence for the SDLE on Fe–C–Mo, Fe–C–Mn and Fe–C–Cr alloys in temperature regions which Bhadeshia terms or might term bainitic is based on experimental measurements made upon ferrite allotriomorphs formed *at* the temperatures discussed. They are not extrapolations.

3. Bhadeshia avers that grain boundary allotriomorphs form by the ledge mechanism; hence Aaronson and his colleagues should not treat their growth as if it takes place by uniform atomic attachment. He also objects to the correction which Bradley and Aaronson made to their data on the thickening kinetics of ferrite allotriomorphs in Fe–C–X alloys for faceting upon the basis of their earlier data [15] on thickening kinetics in Fe–C alloys. He then states that "it is often not obvious that comparative studies involved identical interfaces".

At the present time, the early suggestion of Aaronson [40] that ferrite allotriomorphs have an interfacial structure consisting of alternating areas of partially coherent and disordered type structure appears to remain the best estimate available of the nature of this structure. However, thanks to transformation of the remaining austenite to martensite during quenching to room temperature when isothermal transformation is terminated, there is as yet no satisfactory TEM evidence with which to test this suggestion, or to estimate the proportions of the types of structure present. Even if such data were available, as Trivedi [41] points out a treatment of the growth kinetics of an interface with a mixture of structures has yet to be attempted. Since many allotriomorphs have a moderately smooth morphology, it has become customary to treat their growth kinetics as if they were those of disordered interphase boundaries. Bradley *et al.* [15] made measurements of the thickening and lengthening kinetics of ferrite allotriomorphs in high-purity Fe–C alloys in order to obtain an empirical estimate of the effects of undercooling and carbon concentration upon the deviation of the growth processes and kinetics actually operative from those assumed by the model of uniform atomic attachment to an oblate ellipsoid.

Although these kinetics are slowed down, presumably by facets which must migrate by the ledge mechanism, especially at low carbon concentrations and small undercoolings, with increased undercooling and/or carbon concentration in the alloy these deviations are rapidly reduced. Since the experimental technique used to measure lengthening and thickening kinetics is based on the longest and the thickest allotriomorph in the plane of polish, it is likely that such allotriomorphs will have a somewhat similar arrangement of partially coherent and of disordered areas in different specimens. There seems little reason to anticipate any marked effect of carbon concentration upon these arrangements or, in the dilute alloys used, of X concentration.

At the higher end of our X range and in the alloys often used by the Honeycombe research group, when X is a strong carbide-former, sideplate formation can be suppressed or inhibited, likely by the SDLE [3, 39]. In this circumstance, allotriomorphs can thicken sufficiently so that the slowest growing facet plane (i.e., the one with the largest average inter-ledge spacing) will eventually occupy a large proportion of the interphase boundary area. The ledge structure of the allotriomorphs will then be more clearly revealed, as indeed Honeycombe and coworkers [42] have observed, particularly at later reaction times. However, in our experiments earlier stages of reaction were usually employed, the concentration of X (when a strong carbide-former) was often though not always less and the ledge mechanism appears to have been confined to a smaller scale of operation.

7. Conclusion

In this paper, we have shown that the criticisms which Bhadeshia has made of the solute drag-like effect and the evidence for it are incorrect and/or inappropriate.

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