

# Role of Carbon and Alloying Elements in the Formation of Bainitic Ferrite

M. HILLERT, L. HÖGLUND, and J. ÅGREN

One approach to the prediction of the carbon content of austenite, remaining after the precipitation of bainitic ferrite, is based on the assumption that bainitic ferrite during growth inherits the carbon content of the parent austenite. An alternative approach is based on the assumption that bainitic ferrite grows with a low carbon content and there is no major difference between Widmanstätten ferrite and bainitic ferrite. The two approaches are now compared using information from alloyed steels with considerable amounts of Si, where the formation of cementite is retarded. The former approach does not account for the effect of Mn and fails severely at low alloy contents. The latter approach seems more promising but is not without difficulties. In particular, in order to explain the effects of Cr and Mo, it seems necessary to introduce a kinetic effect, presumably caused by solute drag.

## I. INTRODUCTION

ONE of the controversies about the formation of bainite concerns the role of carbon. Hultgren was probably expressing the general opinion at his time when he in 1926<sup>[1]</sup> proposed that “needles of troostite” first formed as martensite needles, which were then self-tempered. Another opinion was expressed by Robertson in 1929<sup>[2]</sup> who proposed that the growth of the ferritic constituent of bainite is controlled by carbon diffusion. Wever and Lange in 1932<sup>[3]</sup> illustrated his idea with an Fe-C phase diagram where the  $\alpha/\alpha + \gamma$  phase boundary was extrapolated to progressively higher carbon contents at lower temperatures. Evidently, the idea was that bainitic ferrite grows with a carbon content determined by local equilibrium with austenite. In 1946, Zener<sup>[4]</sup> put the first alternative in scientific terms by proposing that bainite could form only below the  $T_0$  line, where thermodynamics would allow ferrite to inherit all the carbon of the parent austenite by partitionless growth. Kinetically, this would be possible only at high growth rates, where there is no time for carbon to escape the migrating interface. On the other hand, after extensive microscopic studies, Hultgren in 1947<sup>[5]</sup> emphasized observations made on upper bainite and proposed that the bainitic transformation starts with growth of Widmanstätten ferrite, which is diffusion controlled because carbon has to partition between ferrite and austenite. The transformation is then completed by sidewise growth of ferrite together with carbide. In 1952, Ko and Cottrell<sup>[6]</sup> reported two observations on bainite, which have been used as arguments for the two opinions, one for each. Their observation of a surface relief supports the similarity with martensite, but their observation of slow growth supports control by carbon diffusion. Since then, some have tried to make the martensitic picture self-consistent by maintaining that the growth is rapid and all the carbon is inherited even though most of it will be lost quickly. They have thus been forced to propose that growth occurs in small but quick steps.<sup>[7]</sup> On the other hand, they have accepted that

Widmanstätten ferrite grows by carbon-diffusion control, although that structure also shows a surface relief. Others have tried to make the other picture self-consistent by arguing that Widmanstätten ferrite, upper bainite, and lower bainite form a continuous series of acicular ferrite.<sup>[8]</sup> The difference between Widmanstätten ferrite and bainitic ferrite is denied by reference to a smooth variation of the growth rate and of the critical carbon content with temperature.<sup>[9]</sup> It should be mentioned that by alloying with Al or Si, it is possible to retard the formation of cementite in bainite, which will then simply consist of plates of ferrite, looking like Widmanstätten plates. Whether they are identical to Widmanstätten plates may be discussed, but in the present work, the term “acicular ferrite” will be used for both, and the critical carbon content of austenite, above which acicular ferrite cannot grow, will be denoted  $WB_s$ .

When the carbide formation is retarded, one can approach a final  $\alpha + \gamma$  state in isothermal heat treatments. The high carbon content of that austenite increases its stability with respect to the martensitic transformation, an effect used in modern TRIP steels. It is thus of considerable practical importance to be able to predict the critical carbon content where the formation of acicular ferrite stops. Of course, the predictions depend on the model chosen, and so far, one has only tried Zener’s model. The model based on growth by carbon diffusion will now be used for the same purpose and the results will be compared.

## II. PROPOSED MECHANISMS

When testing Hultgren’s proposal of growth controlled by carbon diffusion, Hillert<sup>[9]</sup> applied a rate equation to experimental lengthening rates of acicular ferrite. When extrapolating the rates to zero, he found that the critical carbon content for growth did not coincide with the equilibrium line,  $Ae_3$ , an effect directly related to what has later been described as “incomplete transformation.” Hillert proposed that there is a thermodynamic barrier to the growth of acicular ferrite and evaluated its height (curve (a) in Figure 1). The data did not indicate any sharp change between Widmanstätten ferrite at higher temperatures and bainitic ferrite at lower, supporting the proposal that they grow by essentially the same mechanism.

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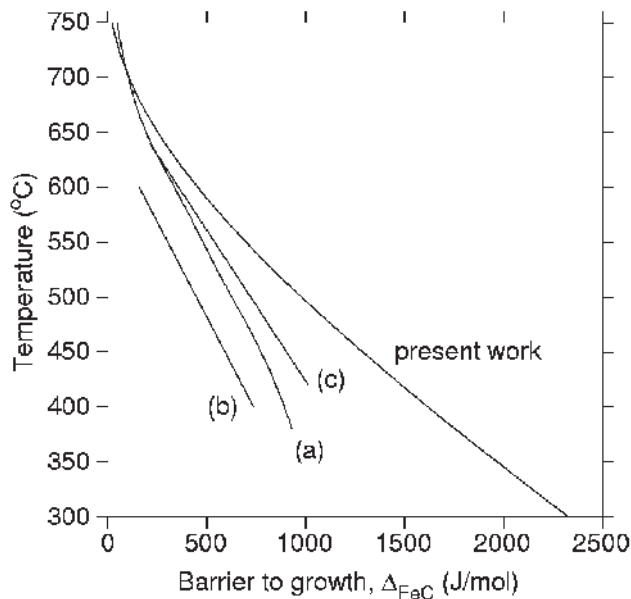


Fig. 1—The recommended barrier for acicular growth of ferrite in Fe-C alloys, compared to previous estimates (a) from Ref. 9, (b) from Ref. 12, and (c) from Ref. 14.

If, on the other hand, bainitic ferrite inherits all the carbon of the parent austenite, then it would seem possible that the entire material could transform to bainitic ferrite, if the steel falls below  $T_0$ , the line of equal Gibbs energy for ferrite and austenite. This is not the case and in his picture of the bainite formation Zener explained this fact by suggesting that each new plate of bainitic ferrite inherits all the carbon of the parent austenite but quickly loses most of it to the remaining austenite. When the austenite composition has thus moved to  $T_0$ , there are thermodynamic reasons why diffusionless transformation to bainite cannot proceed.

From measurements of the  $B_s$  temperature, one can take the critical carbon content directly as the average carbon content of the steel. By preventing the formation of cementite with Al or Si, it could also be evaluated from the carbon content of the austenite remaining at the end of the bainite reaction at any temperature. One may simply evaluate the carbon content from the volume fraction of the remaining austenite or its lattice parameter. From a single alloy, transformed to carbide-free bainite at different temperatures, one can thus obtain a series of carbon contents and according to Zener's suggestion all those values should fall on the  $T_0$  line, calculated for the actual alloy content.

Le Houillier *et al.*<sup>[10]</sup> later proposed that the line of equal Gibbs energy should be calculated with an additional term for ferrite due to strain energy. The critical carbon content would thus differ from the predictions of the  $T_0$  line. This additional proposal was accepted by Bhadeshia and Edmond<sup>[11]</sup> who estimated the effect of strain and interfacial energy to 270 J/mol and denoted the calculated line  $T_0'$ . They evaluated the carbon content of the remaining austenite from the volume fraction at various temperatures for a particular steel and reported fair agreement with the  $T_0'$  line. Later, Bhadeshia<sup>[12]</sup> extended the analysis to the large number of steels for which Steven and Haynes<sup>[13]</sup> had determined the  $B_s$  temperature. For each one, he calculated the difference in Gibbs energy for the ferritic and austenitic states at

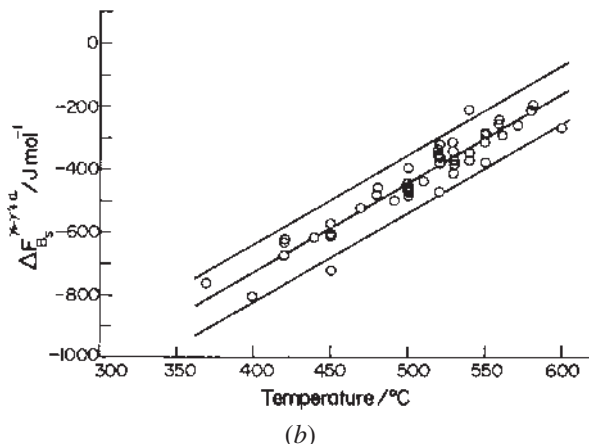
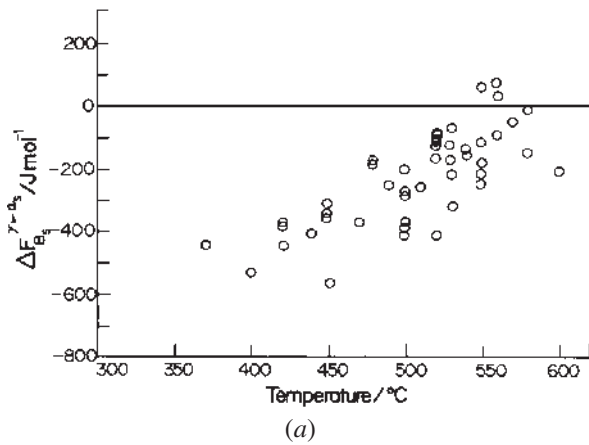


Fig. 2—Evaluation of barriers for growth of acicular ferrite using information on  $B_s$ : (a) for formation without diffusion of carbon and (b) for formation with partitioning of carbon (reproduction from Ref. 14).

the  $B_s$  temperature, assuming that they would have the same carbon content, presumably hoping to find values around  $-270$  J/mol. Figure 2(a) is a reproduction from his work and demonstrates that the data showed a very strong scatter from slightly positive values to values below  $-600$  J/mol. It is evident that the  $T_0'$  concept did not apply.

Bhadeshia then calculated the change in Gibbs energy if ferrite would form with a low carbon content as proposed by Hultgren, finding that the scatter had decreased to half (Figure 2(b)). Bhadeshia represented those data with the middle line in Figure 2(b) and denoted the Gibbs energy change by  $\Delta F_N$ . In a new assessment, he later denoted it by  $\Delta G_N$ .<sup>[14]</sup> His two estimates are compared with Hillert's in Figure 1 and his second assessment (curve c) is in rather good agreement, especially at the higher temperatures. However, in contrast to Hillert, Bhadeshia maintained that bainitic ferrite grows with a high supersaturation of carbon and suggested that the  $\Delta F_N$  quantity, which is evaluated for partitioning of carbon, represents the barrier for nucleation, but is not relevant to the growth process. In any case, that suggestion cannot apply to Hillert's values, which were extracted from information on growth. According to Bhadeshia's suggestion, the agreement with Hillert's values would thus be incidental. Bhadeshia actually suggested that  $\Delta F_N$  is a "universal curve for nucleation" of Widmanstätten ferrite, bainitic ferrite, and martensite, and

the nucleus should thus consist of low-carbon ferrite in all three cases (Figure 10 in his article).<sup>[12]</sup>

When Bhadeshia calculated the driving force for growth without carbon partitioning at  $B_s$  for another steel, he obtained agreement with a  $T_0'$  line calculated when the Gibbs energy for ferrite was increased with a value of 400 J/mol, a value that he has since used instead of 270 J/mol as a constant barrier for growth of bainitic ferrite but not for Widmanstätten ferrite.<sup>[14]</sup>

### III. EFFECT OF Mn

In 1990, Usui *et al.*<sup>[15]</sup> studied the effect of Mn at a constant Si content of 1.5 mass pct. They measured the lattice parameter and used an equation to relate it to the carbon content. Several such equations have been proposed, but they differ appreciably because of experimental difficulties caused by austenite not being stable at room temperature. In 1953, Roberts compiled the information available and gave an equation.<sup>[16]</sup> In 1978, Cullity<sup>[17]</sup> transformed it from kX units to Ångström units. At the same time, Nishyama<sup>[18]</sup> gave an equation that yielded somewhat higher carbon contents. However, already in 1969, Ruhl and Cohen<sup>[19]</sup> realized that the lattice parameter for pure austenitic iron should probably be appreciably higher, and in 1970, Dyson and Holmes<sup>[20]</sup> used an even higher value, which was later supported by the results of a study by Onink *et al.*<sup>[21]</sup> in 1993. Onink *et al.* made a careful study of the temperature dependence of the lattice parameter and gave an equation containing the temperature dependence. For room temperature, it is very similar to the equation by Dyson and Holmes, which is  $0.0033C = a - 0.3578$ , where C is the mass pct carbon and  $a$  is the lattice parameter in nanometers. This equation was recently accepted by Sugimoto *et al.*<sup>[22]</sup> and will be used in the present work. Reported data obtained by using other equations were recalculated before being used in the present work, and the resulting carbon contents were invariably lower than those reported originally. It should be noted that the effect of alloying elements on the lattice parameter is generally neglected because it is probably not larger than the experimental uncertainty. It was also neglected in the present work.

Figure 3 shows the results from Usui *et al.*<sup>[15]</sup> at 400 °C. The figure demonstrates a very strong dependence on the Mn content and indicates that the value without Mn would be very high. This is supported by some values reported by Tsuzaki *et al.*<sup>[23]</sup> for a steel without Mn but with 2 mass pct Si, presented as circles. In fact, those values refer to 450 °C and the value at 400 °C should be even higher. According to Bhadeshia's proposal, the results of Usui *et al.* could be represented by the  $T_0'$  line, but Figure 3 demonstrates that the slope of that line is much too small. The  $T_0$  line is also shown in Figure 3. It predicts values about 0.2 mass pct C higher, but still the same small dependence on the Mn content. It will thus be interesting to compare this with predictions from the model based on growth controlled by carbon diffusion.

All calculations in the present work were made with the Thermo-Calc databank system<sup>[24]</sup> and its database TCFE2000. The value of  $T_0$  was calculated for a diffusionless transformation, and  $T_0'$  was determined in the same way but after increasing the Gibbs energy of ferrite by 400 J/mol. In Sections IV–VI, several calculations of  $WB_s$  will be presented. They were pro-

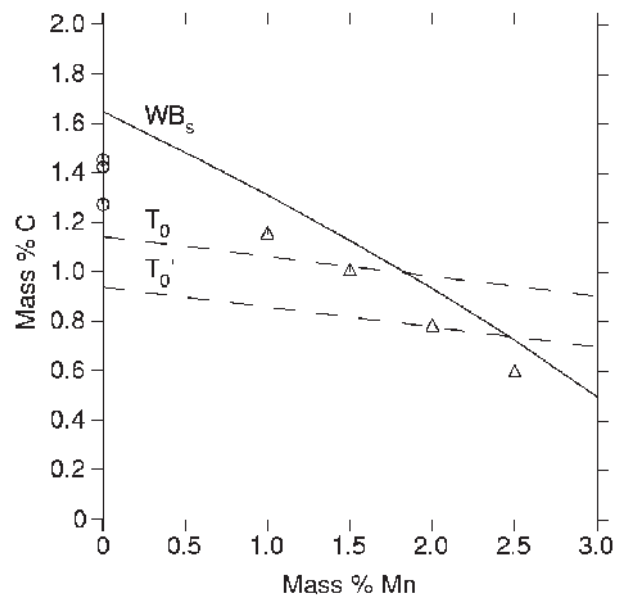


Fig. 3—The critical carbon content as a function of the Mn content at 1.5 mass pct Si at 400 °C. Triangles are from Ref. 15 and circles from Ref. 23.

duced from the same databank and database and under the assumption of paraequilibrium after increasing the Gibbs energy of ferrite with the energy barriers soon to be discussed.

### IV. THERMODYNAMIC BARRIER TO DIFFUSIONAL GROWTH

According to curve (a) in Figure 1, the barrier for diffusion-controlled growth varies with temperature and a new estimate of that quantity will now be made. The previous assessment was based on steels with some amounts of alloying elements. The new analysis is based on the experimental information from laboratory Fe-C alloys. As before,<sup>[9]</sup> the  $W_s$  or  $B_s$  temperature was evaluated by extrapolating the lengthening rate,  $v$ , to zero using the quantity  $(vc^0)^{0.5}$ , which should yield an approximately linear relationship according to the Zener–Hillert equation,<sup>[8]</sup> where  $c^0$  is the initial carbon content of the steel. Figure 4 shows data at 700 °C and some additional data at 709 °C.<sup>[9]</sup> A straight line representation for 700 °C has been drawn, but it is evident that there is a considerable uncertainty in the extrapolated value of  $c^0 = 0.76$  mass pct C at  $v = 0$ . Figure 5 shows data from 300 °C,<sup>[25]</sup> and again, it is evident that the extrapolated value, here, 1.94 mass pct C, has a considerable uncertainty due to the long extrapolation. Nevertheless, these two points were accepted for the present analysis. At intermediate temperatures, there seems to be no information at sufficiently low lengthening rates to justify extrapolation to zero. The best alternative seemed to be the determination of the critical carbon content in the remaining austenite through measurements of the lattice parameter. For such measurements, it is necessary to avoid the formation of carbides, and information from an Fe-C-Si alloy with 2.01 mass pct Si was used.<sup>[23]</sup> Using the equation by Dyson and Holmes and considering that Si decreases the lattice parameter, this information on the lattice parameter was used to estimate a value of 1.5 mass pct C at 450 °C. In Figure 6, the three points are plotted directly in

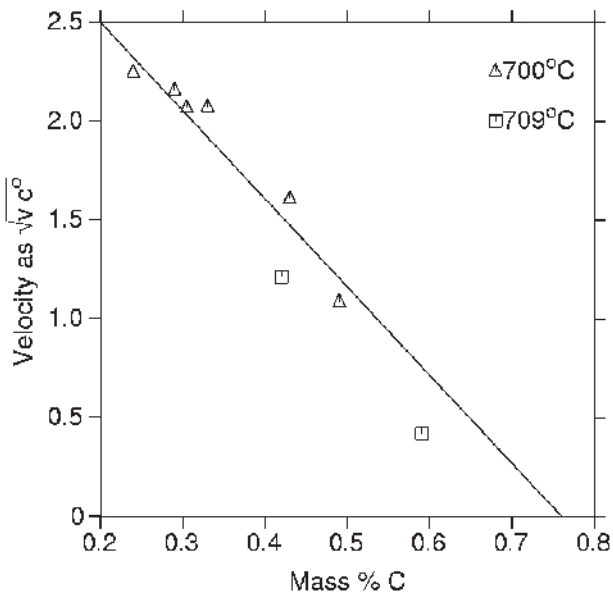


Fig. 4—Extrapolation of the rate of lengthening at 700 °C to the value zero, using the Zener-Hillert equation. Experimental data are from Ref. 9.

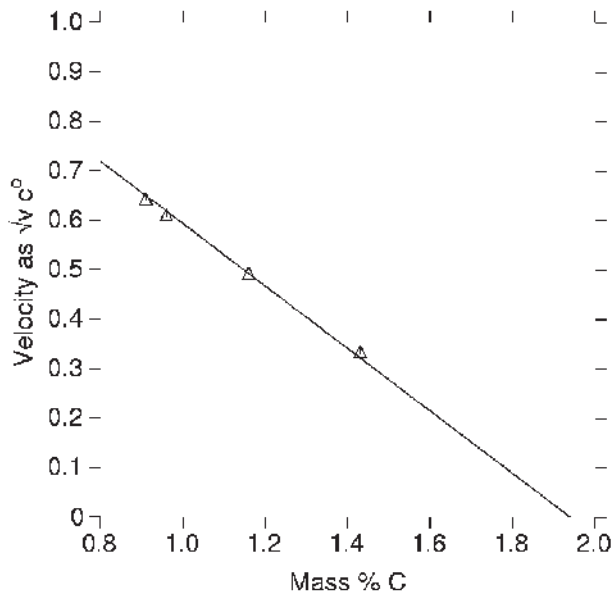


Fig. 5—Extrapolation of the rate of lengthening at 300 °C to the value zero, using the Zener-Hillert equation. Experimental data are from Ref. 25.

the Fe-C phase diagram and are compared with  $Ae_3$ , the line representing austenite in equilibrium with ferrite.

From the three points, the driving force for the formation of ferrite under partitioning of carbon was evaluated using the thermodynamic data on Fe-C from Gustafson.<sup>[26]</sup> The values of 107, 1283, and 2329 J/mol of iron were obtained at 700 °C, 450 °C, and 300 °C, respectively. This quantity will now be denoted  $\Delta$  without the subscript  $N$  instead of  $\Delta F_N$  or  $\Delta G_N$ , because it will not be interpreted as the driving force for nucleation. A spline function was applied in order to get a smooth variation with temperature. In order to give the function a reasonable extrapolation below 300 °C, a fictitious value of 6000 J/mol was chosen at -200 °C. The

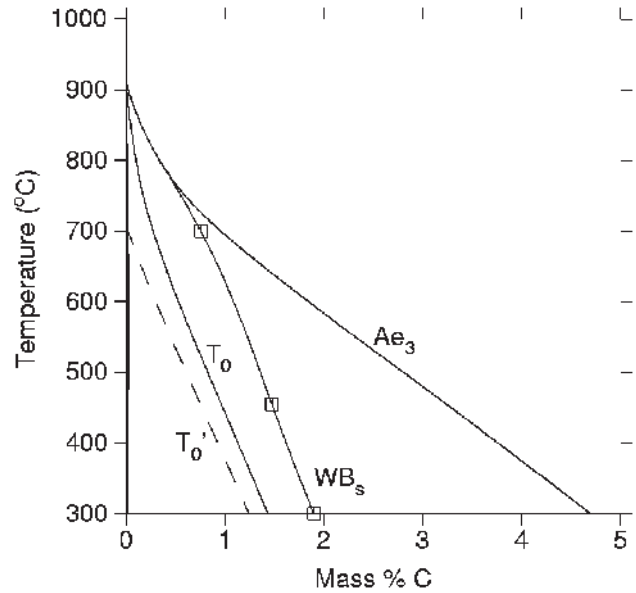


Fig. 6—The recommended  $WB_s$  line compared with three other lines, proposed to be the critical limit for acicular growth of ferrite in Fe-C alloys. The squares show the experimental information used in fitting the  $\Delta$  function from which the  $WB_s$  line was calculated.

shape of the curve at high temperatures indicates that it should decrease further above 700 °C. Quite arbitrarily, the function was made to approach zero by fitting it to a value of  $\Delta = 4$  J/mol at 800 °C and introducing the value zero at all temperatures above 800 °C. It should be emphasized that the function is not recommended to be used much below 300 °C or much above 700 °C. The final curve is presented in Figure 1 together with the previous estimates.

Using the  $\Delta$  function and Gustafson's thermodynamic data, it was now possible to calculate  $WB_s$  as a function of temperature for the Fe-C system and to compare with the lines for  $Ae_3$ ,  $T_0$ , and  $T_0'$  (Figure 6). It is evident that the three experimental points on  $WB_s$  could not be represented by the  $T_0$  line, and the  $T_0'$  line would yield an even stronger discrepancy. It can be concluded that Zener's proposal cannot be applied to the binary Fe-C system and Bhadeshia's introduction of an energy barrier of 400 J/mol makes the discrepancy even larger.

## V. NEW PREDICTIONS OF THE EFFECT OF ALLOYING ELEMENTS

For alloyed steels, there are several studies of the critical carbon content in the austenite, evaluated from the volume fraction that remains after the transformation to carbide-free bainite has stopped. They usually cover a wide range of temperature for each steel, starting with the  $B_s$  temperature. Figure 7 compares such information for a steel 0.43C;2.12Si; 3.00Mn<sup>[11]</sup> with the  $WB_s$  curve calculated for that alloy content. The agreement with experimental information seems satisfactory. Comparison with Figure 6 shows that these alloying elements have decreased the carbon content of  $WB_s$  at 300 °C from 1.94 to 0.68 mass pct by their effects on the thermodynamic properties. The  $T_0'$  line is shown as a dashed line and has decreased from 1.24 mass pct C in Figure 6 to 1.00 mass pct C at 300 °C. Compared to the data,  $T_0'$  falls at carbon contents about 0.2 mass pct too high. Figure 8 gives the comparison

with experimental data for a steel 0.39C;2.05Si;4.08Ni.<sup>[27]</sup> Due to the large experimental scatter, these data can be fitted equally well with the  $WB_s$  and  $T_0'$  lines, but the temperature dependence is best described by the  $WB_s$  line. It should be emphasized that Bhadeshia *et al.* use a different database and their  $T_0'$  lines are closer to the experimental information in Figures 7 and 8. Before clarifying which database is most correct, the information in these diagrams cannot be used in arguments for one model or the other.

The calculated line for  $WB_s$  as a function of the Mn content at 1.5 mass pct Si is plotted in Figure 3 and it describes the experimental variation with Mn content according to

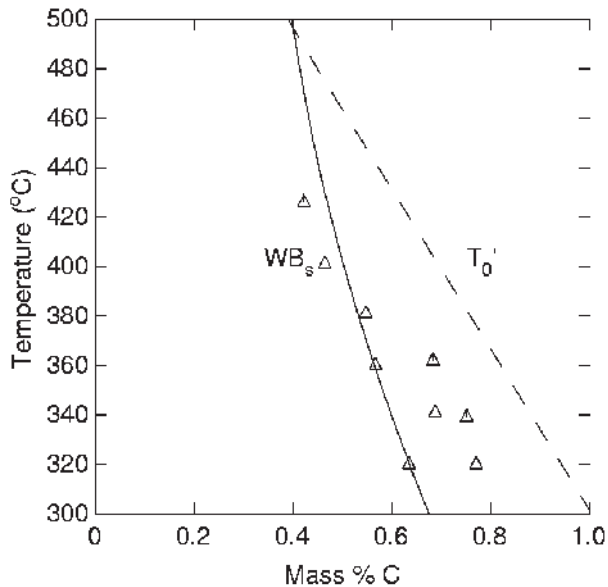


Fig. 7—Carbon content of remaining austenite as a function of temperature of a steel with 0.43 mass pct C, 2.12 mass pct Si, and 3.00 mass pct Mn. Experimental points are from Ref. 11.

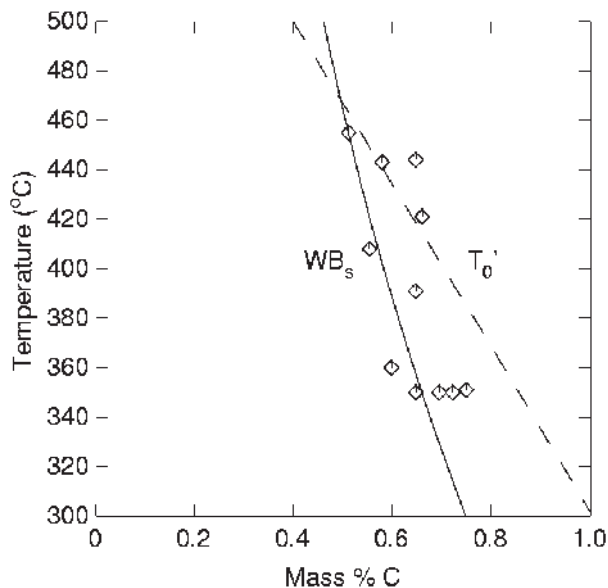


Fig. 8—Carbon content of remaining austenite as a function of temperature of a steel with 0.39 mass pct C, 2.05 mass pct Si, and 4.08 mass pct Ni. Experimental points are from Ref. 27.

Usui *et al.*<sup>[15]</sup> very well but falls above the experimental points. However, more recent information from the same group indicates that the data in Figure 3 had a systematic error. Figure 9 shows the variation with temperature at 1.51 mass pct Mn and 1.51 mass pct Si according to new data.<sup>[28]</sup> There is excellent agreement with the calculated  $WB_s$  line and a disagreement of 0.2 to 0.3 mass pct C with the  $T_0'$  line. Furthermore, Figure 10 gives even more recent data,<sup>[29]</sup> to be compared with Figure 3. The values for 1.5 mass pct Mn are very well represented for both 375 °C and 450 °C but the scatter in the dependence on the Mn content is much larger than for the earlier data used in Figure 3.

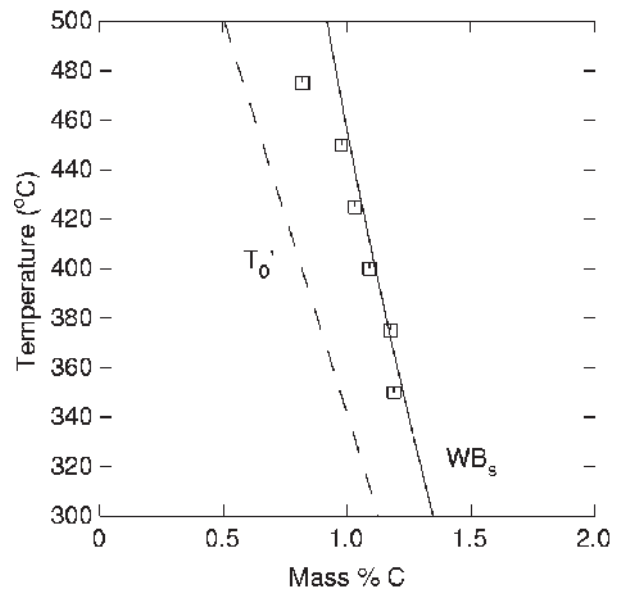


Fig. 9—Carbon content of remaining austenite in a steel with 1.51 mass pct Si and 1.51 mass pct Mn. Experimental data are from Ref. 28.

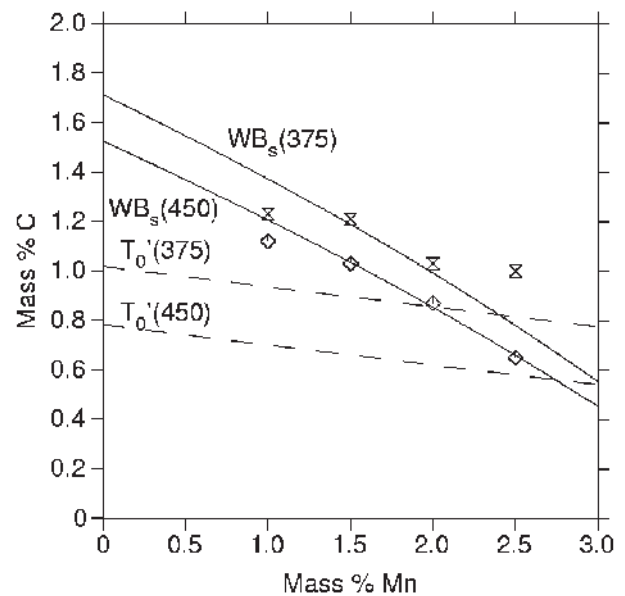


Fig. 10—Carbon content of remaining austenite as a function of the Mn content at 1.5 mass pct Si and at two temperatures. Experimental points are from Ref. 29.

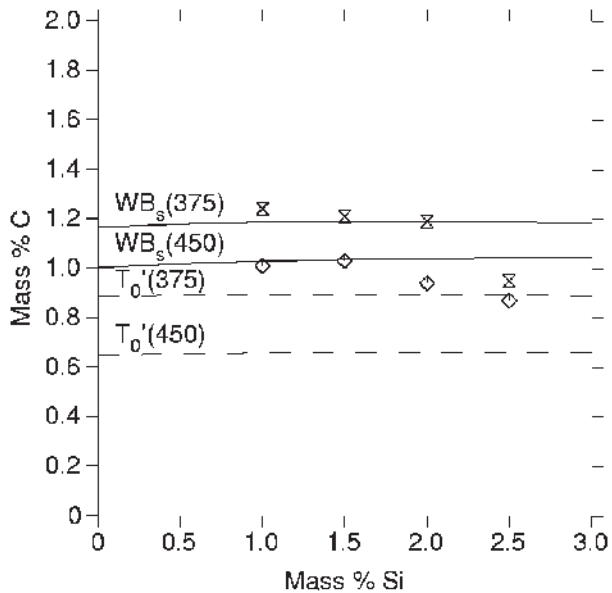


Fig. 11—Carbon content of remaining austenite as a function of the Si content at 1.5 mass pct Mn and at two temperatures, 375 °C and 450 °C. Experimental points are from Ref. 29.

Figure 11 gives a comparison with data for the variation with the Si content at 1.5 mass pct Mn.<sup>[29]</sup> The calculated  $WB_s$  lines represent the data very well in the range 1 to 2 mass pct Si, but there is a deviation at higher Si contents. The predicted variation with composition, *i.e.*, the slope of the  $WB_s$  line, which here is very small, is of a purely thermodynamic origin and should be correct if the proper model is used. It could be speculated whether the deviation at higher Si contents is due to a change of the mechanism of the transformation or to experimental difficulties. In any case, the  $WB_s$  approach predicts that the effect of Si is negligible, and this is confirmed experimentally up to 2 mass pct Si.

It is interesting to note that in all these examinations of information from various steels, there was no indication of a systematic difference between the data obtained from the lattice parameter, after applying the equation by Dyson and Homes, and previous data obtained from the volume fraction. It should also be noted that Bhadeshia's database would displace the  $T_0'$  lines in Figures 9 and 10 even further to lower carbon contents and increase the difference to the experimental information.

## VI. EFFECT OF Cr AND Mo

For Cr and Mo, the results of the analysis of data assuming diffusion control were different. For Cr, the experimental information on the  $B_s$  temperature for steels with 3 pct Cr was taken from the classical work by Lyman and co-workers<sup>[30,31,32]</sup> and a more recent study.<sup>[33]</sup> For each steel, the  $\Delta$  value was calculated at the experimental  $B_s$  temperature from the chemical analysis of the steel, again assuming paraequilibrium and using the same database. In Figure 12, the results are compared with the  $\Delta$  function for the Fe-C system, *i.e.*, the curve presented in Figure 1 but now denoted  $\Delta_{FeC}$ . The data cover a wide temperature range because the carbon content of the steels varied from 0.08 to 1.28 mass pct and the experimental  $B_s$  thus fell at widely different temperatures. The deviation of these

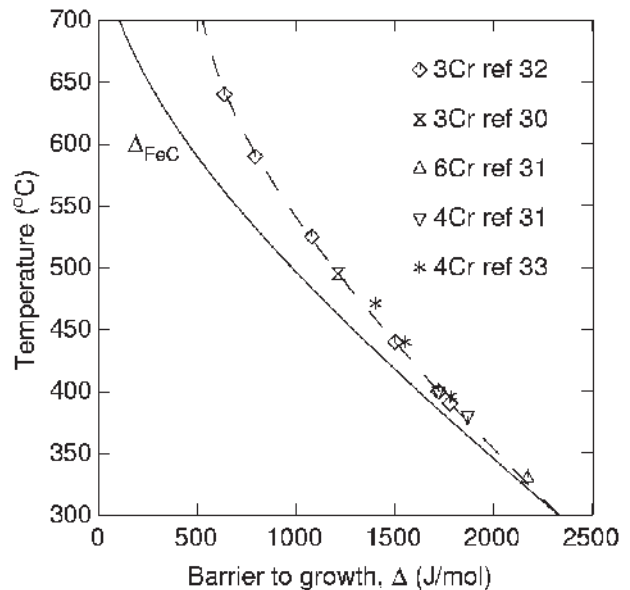


Fig. 12—The barrier to acicular growth of ferrite. The full line is for Fe-C alloys. The dashed line is fitted to the experimental points for steels with about 3 mass pct Cr.

experimental points from the curve for the Fe-C system is positive, which implies that the critical carbon content of the austenite in the Cr steels should be lower than predicted by a purely thermodynamic effect. The deviation seems to increase with temperature and we decided to represent the deviation with a function  $\Delta_{Cr} = 0.35(T - 573)c_{Cr}^0$ , where  $c_{Cr}^0$  is the mass pct Cr in the steel and  $T$  is the temperature in kelvin. A curve for  $\Delta = \Delta_{FeC} + \Delta_{Cr}$  at 3 mass pct Cr is included in Figure 12 as a dashed line and represents those experimental data quite well. In order to have some information from the lowest temperatures, two experimental points from steels with about 4 and 6 mass pct Cr were used. It should be noted that below 300 °C, the value zero is proposed instead of the  $\Delta_{Cr}$  function, which would there turn negative. It should further be mentioned that the function is not intended for use at Cr contents appreciably higher than 3 mass pct. At the higher temperatures, the relative effect seems to decrease at higher Cr contents.

Figure 13 is a corresponding plot for Mo contents of about 1 mass pct. At the higher temperatures, the information comes from a study of the final fraction of ferrite in an alloy with 0.93 mass pct Mo at different temperatures.<sup>[34]</sup> The carbon content of the remaining fraction of austenite was evaluated using the lever rule and the initial carbon content. The information at the lower temperatures comes from a steel 0.44C; 1.74Si; 0.67Mn; 0.39Cr; 0.83Mo; 0.09V, for which the volume fraction of austenite was measured at various temperatures.<sup>[27]</sup> It is well known that V has the same kind of effect on the time-temperature-transformation (TTT) diagram as Cr and Mo, but its effect was not analyzed in the present work due to the low contents in the analyzed steels. It was simply assumed that it has exactly the same effect as Mo. Again, the diagram seems to indicate that the deviation from the curve for Fe-C increases with the temperature, and the function for Mo was obtained as  $\Delta_{Mo} = 0.8(T - 523)c_{Mo}^0$ . The curve for  $\Delta = \Delta_{FeC} + \Delta_{Mo}$  at 0.93 mass pct Mo is presented as a dashed line. It should not quite represent the experimental values in the lower temperature range because the effect of the Cr con-

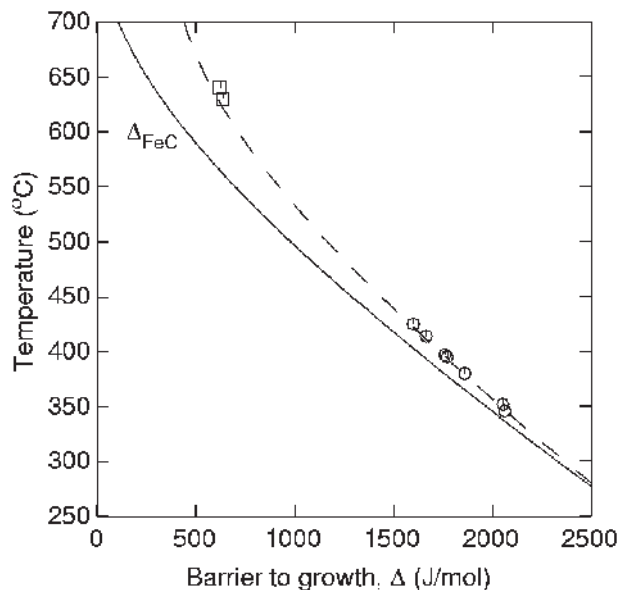


Fig. 13—The barrier to acicular growth of ferrite. The full line is for Fe-C alloys. The experimental points are for steels with about 1 mass pct Mo from Ref. 34, squares, and Ref. 27, circles.

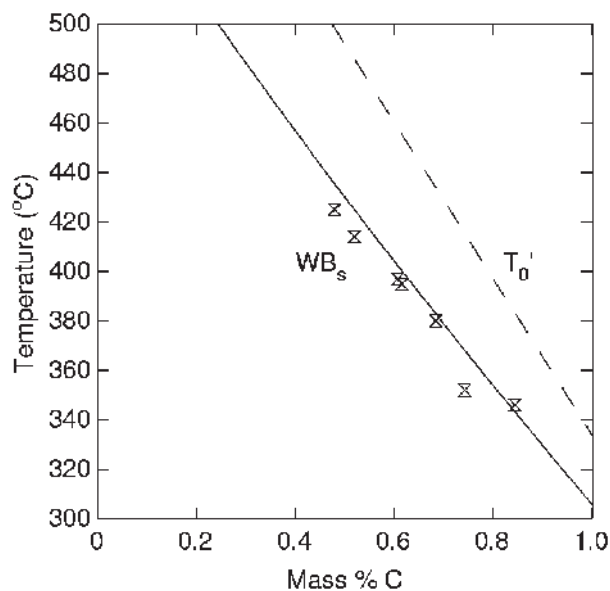


Fig. 14—Carbon content of remaining austenite as a function of temperature for a steel with 0.44 mass pct C, 1.74 mass pct Si, 0.67 mass pct Mn, 0.39 mass pct Cr, 0.83 mass pct Mo, and 0.09 mass pct V. Experimental points are from Ref. 27.

tent was not included in the calculation of the line. However, that effect is rather small here. It should be noted that below 250 °C, the value zero is proposed instead of the  $\Delta_{\text{Mo}}$  function. It should further be mentioned that the function is not intended for use at Mo contents appreciably higher than 1 mass pct. The relative effect decreases at higher Mo contents. In order to test the description thus obtained, it was applied to the steel 0.44C;1.74Si;0.67Mn;0.39Cr;0.83Mo;0.09V,<sup>[27]</sup> and the good fit demonstrated by Figure 14 indicates that the present analysis is self-consistent. It should be mentioned that the

$T_0'$  line would move considerably closer to the experimental data in Figure 14 if calculated with Bhadeshia's program and database.

## VII. DISCUSSION

It should be emphasized that the new approach for predicting the critical carbon content for acicular growth of ferrite as well as Bhadeshia's modification of Zener's proposal are both quite empirical because experimental data have been used for evaluating Gibbs energy barriers. In Bhadeshia's case, it was  $\Delta F_N$ , the barrier for nucleation, and the value 400 J/mol, the barrier for growth. In the present case, it was  $\Delta_{\text{FeC}}$ , the barrier for growth in Fe-C alloys. On the other hand, both approaches include the thermodynamic effect of alloying elements with no adjustable parameter and are thus predictive in this sense. The success of the present method in predicting the effect of the strong austenite stabilizers Mn and Ni lends strong support to the proposal that acicular ferrite grows with a low carbon content. It is interesting to note that the thermodynamic effect of the strong austenite stabilizers, Mn and Ni, would be much weaker if ferrite is assumed to inherit the carbon content of the parent austenite. The strong effect of Mn, observed experimentally and demonstrated in Figure 3, may thus be taken as a decisive argument against Zener's proposal that bainitic ferrite grows with a high supersaturation of carbon, which was later used in Bhadeshia's approach.

It should be mentioned here that Takahashi and Bhadeshia,<sup>[35]</sup> when discussing Usui's data, compared it with the  $T_0$  line rather than the  $T_0'$  line and argued that "The  $T_0$  and  $T_0'$  curves are in fact only slightly different in carbon concentration . . .," and then they concluded that "it is a reasonable assumption to neglect the strain energy term. . .", *i.e.*, Bhadeshia's 400 J/mol barrier. However, Figure 3 shows that the difference between  $T_0$  and  $T_0'$  is about 0.2 mass pct carbon, which is substantial. Furthermore, Bhadeshia's conclusion that "the effect of manganese is also well represented by the thermodynamically calculated  $T_0$  curve" is difficult to accept. It seems to predict only a fifth of that dependence. Due to the difference in slope of the  $WB_s$  line on one hand and the  $T_0$  and  $T_0'$  lines on the other, the intersections of the  $T_0'$  and  $T_0$  lines with the  $WB_s$  line occur at different Mn contents, 2.5 and 1.7 mass pct Mn, respectively. Bhadeshia could thus improve his agreement by using the  $T_0$  line when discussing Usui's TRIP steel with the typical value of 1.5 mass pct Mn but using the  $T_0'$  line when discussing steels with 3 mass pct Mn or 4 mass pct Ni.

The thermodynamic effect of ferrite stabilizers is predicted to be very small and experimental information on Si seems to confirm this. The same may be expected for Al. However, it appears that the effects of Cr and Mo cannot be predicted very accurately from the thermodynamic properties alone. It is suggested that they give a strong solute-drag effect and Figures 12 and 13 indicate that this effect grows stronger at higher temperatures. The empirical expressions for the additional effect of Cr and Mo, presumably caused by solute drag, should only be regarded as very preliminary, but they may give a guideline for the future development of a treatment for the solute drag.

So far, none of the two approaches has been adapted to take into account the possible effect of the carbon content of the steel through the effect of the volume fraction of the

remaining austenite, which has been proposed by Quidort *et al.*<sup>[36]</sup> Such an effect could be included by allowing the energy barrier to vary with the fraction of ferrite, but no attempt was made in the present work to predict this effect. Detailed experimental studies would be required in order to evaluate this possible effect, because, if it exists, it would most probably vary with the spatial distribution of ferrite and austenite as well. Actually, in all of Figures 7, 8, and 14, the fraction of ferrite varies with temperature, starting with 0 pct at the highest temperature. Figure 14 gives no indication of an effect of the fraction of ferrite, and, unfortunately, in Figures 7 and 8, the experimental scatter is too large to allow any conclusion on this question.

## VIII. CONCLUSIONS

The new approach for predicting the critical carbon content of austenite, where Widmanstätten ferrite or bainitic ferrite can no longer grow, is capable of predicting the strong effect of the austenite stabilizers Mn and Ni and may thus be taken as strong support for the proposal that bainitic ferrite grows with a low carbon content. The failure of Bhadeshia's approach to predict the critical carbon content for bainite in the Fe-C system in Figure 6 and the effect of Mn in Figure 3 are strong arguments against Zener's proposal that bainitic ferrite grows with a high supersaturation of carbon.

Admittedly, there may be a considerable uncertainty in much of the data used in the present work, *e.g.*, due to the uncertainty in the relation between lattice parameter and carbon content of austenite at room temperature. However, the agreement with experimental data, after applying the equation by Dyson and Holmes, indicates that the present approach could in any case be of practical use as a means of replacing experimental measurements of the lattice parameter with predictions.

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