

Thermodynamic analysis of isothermal transformation diagrams

H. K. D. H. Bhadeshia

A thermodynamic method has been developed to allow the prediction of isothermal transformation diagrams, starting simply from a knowledge of the chemical composition of the steel concerned. The method has been extensively tested and has been shown to be capable of faithfully reproducing the critical 'bay region' of time-temperature-transformation (TTT) curves. The TTT diagram has been treated as being composed of two overlapping 'C' curves, one representing the diffusional polygonal-ferrite and pearlite transformations, and the other representing the displacive Widmanstätten ferrite and bainite reactions. It is possible to predict relative shifts in these component curves, as a function of alloying element content, thus making the technique potentially useful in theoretical steel design. While the analysis is formally based on Russell's theory of incubation periods, it is believed that a number of difficulties prevent a fundamental interpretation of the results. MS/0696

© 1982 The Metals Society. Manuscript received 2 March 1981; in final form 9 July 1981. The author is in the Department of Metallurgy and Materials Science, University of Cambridge.

While thermodynamic methods have been widely used in assessing and predicting the influence of alloying elements on phase equilibria in steels, isothermal transformation curves have received little similar attention. Hence it is not possible to generate reliably time-temperature-transformation (TTT) diagrams for steels of arbitrary composition, assuming the existence of suitable thermodynamic data. The lack of detailed understanding about the nature of nucleation has hindered the investigation of such diagrams, although there have been a number of notable attempts at rationalizing TTT curves.

In considering the role of nucleation in hardenability, Sharma and Purdy¹ indicated that the incubation periods normally associated with TTT diagrams (i.e. the time period before the onset of a detectable amount of isothermal transformation, τ) can be reasonably described in terms of Russell's linked-flux analysis,^{2,3} where the incubation period is defined as the time τ_s taken to establish a steady-state nucleation rate. Sharma and Purdy managed to explain successfully the relative reaction-start times associated with seven low-alloy steels, although an implicit assumption in their analysis was that the same nucleation process applies to all isothermal transformations in steels.

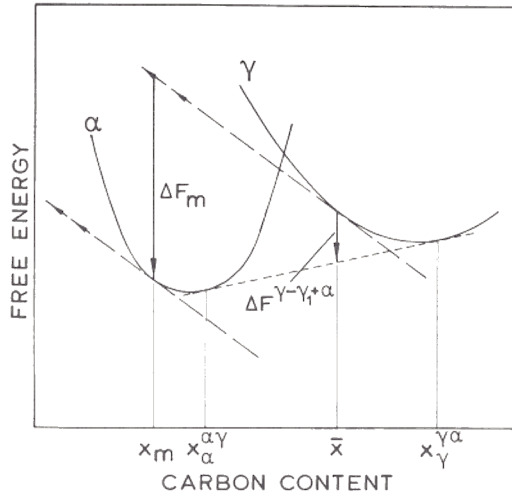
This assumption is equivalent to fitting a unique 'C' curve to all reactions above the martensite-start temperature M_s , and was also used by Kirkaldy *et al.*⁴ in their empirical analysis of low-alloy steel TTT curves. Both these attempts failed to predict the existence of 'bays' in the vicinity of the bainite-start temperature; these bays are regions of the TTT curves where the reaction-start time is significantly greater than that associated with temperatures immediately above or below the cusped region. Experiments indicate that in (low-alloy) steels containing relatively large quantities of alloying elements, the bay is replaced by a break in the TTT diagram, so that the overall appearance becomes that of two C curves separated by a 'stasis region' where no transformation occurs despite prolonged heat treatment.

Various qualitative 'solute-drag' theories have been proposed to account for these bays,^{1,5} but have not been adequately established or shown to be generally applicable. On the other hand, it is becoming increasingly clear that TTT diagrams should be correctly interpreted as being composed of at least two separate C curves, one of which represents diffusional transformations (equiaxed-ferrite and pearlite) and the other, displacive reactions (Widmanstätten ferrite and bainite). Varying degrees of overlap between these curves could then generate the forms of TTT diagrams observed experimentally.⁶ The temperature corresponding to the upper part of the shear transformation C curve is often called the bainite-start temperature B_s , although it strictly refers to the point at which the nucleation of ferrite that grows displacively first becomes possible;⁷ hence it may correspond either to the Widmanstätten-start W_s or the B_s temperature, and can be satisfactorily rationalized⁷ in terms of isothermal-martensite nucleation theory.^{8,9} Bearing these concepts in mind, it was the purpose of this work to analyse thermodynamically isothermal transformation diagrams in order to achieve a useful degree of predictability, generality, and accuracy. It should be noted, however, that the assumption of separate C curves is not crucial to the analysis since, in the event of default, the results should indicate identical descriptive parameters for both curves. In the present work, attention is focused on the reaction-start times, since the thermodynamic calculation of W_s , B_s , and M_s has been dealt with elsewhere.^{7,10,11}

METHOD

Assuming the applicability of classical nucleation theory, neglecting strain energy, and using his theory² for incubation periods, Russell³ obtained several expressions for calculating τ_s for a variety of grain-boundary nucleation situations. These expressions had the general form

$$\tau_s \propto \frac{T}{(\Delta F_m)^p D} \quad (1)$$



1 Schematic diagram illustrating free energy changes involved during nucleation and growth of ferrite

where

- T = absolute temperature
- D = an effective diffusion coefficient related to boundary or volume diffusion, depending on the coherency state of the nucleus concerned
- ΔF_m^v = the maximum *volume* free energy change accompanying the formation of a nucleus in a large amount of matrix phase
- p = an exponent whose magnitude is a function of the nature of the nucleus. Russell obtained $p = 2$ for a coherent nucleus and $p = 3$ for an incoherent one.

Equation (1) has a fairly straightforward format in the sense that τ_s is intuitively expected to be a function of T , ΔF_m^v , and D . Furthermore, equation (1) is very similar (with $p = 1$) to the law describing interfacially controlled growth,¹² in which case D refers to the thermally activated transfer of atoms across the transformation interface. Emphasizing then the generality of the form of equation (1), we may, perhaps with some confidence, use this relationship in a purely phenomenological sense and avoid the choice of any particular nucleus model or even any specific set of events which can lead to the existence of incubation periods. The quantities p and D can then be treated as disposable parameters whose magnitudes may be fixed by curve fitting to experimental data. This approach is believed to be necessary in view of the numerous important assumptions that have to be made when applying equation (1) to data taken from TTT curves. For instance, while τ is likely to be a good approximation for τ_s , no real justification can be given for this assumption. Furthermore, it is unlikely that the nucleation of Widmanstätten ferrite and bainite can be properly described in terms of classical nucleation theory,⁷ since it appears that the activation energy for nucleation is a linear function of the driving force. In addition, little is known about the detailed shape or the state of coherency of the operative nucleus.

In spite of all these complications it seemed reasonable to associate any thermally activated nucleation process with a relationship of the form of equation (1), irrespective of the detailed nature of the 'fluctuations' involved in the growth of an embryo to critical size. However, this method necessarily restricts the fundamental interpretation of any ensuing results, and at worst amounts to empiricism, but has the potential advantage of validating the assumptions

involved, should the best-fit parameters turn out to be 'sensible'.

Referring to equation (1), and using the theory of diffusion coefficients,¹³ we obtain

$$D \propto \exp(S/R) \exp(-Q/RT) \dots \dots \dots (2)$$

where S is the activation entropy for diffusion and Q is the activation enthalpy for diffusion. Substituting this result into equation (1), assuming $\tau = \tau_s$, and multiplying ΔF_m^v by the molar volume of ferrite, we get

$$\ln [(\Delta F_m)^p \tau / T] = Q/(RT) + C_1 \dots \dots \dots (3)$$

where ΔF_m is the chemical free energy change accompanying the formation of 1 mol of nucleating phase in a large amount of matrix phase and C_1 is a constant. Optimum values of p and Q may then be obtained by substituting experimental values of T , ΔF_m , and τ , and systematically varying p until the linear correlation coefficient for equation (3) attains an optimum value.

CALCULATION OF CHEMICAL FREE ENERGY CHANGE FOR NUCLEATION

The significance of the free energy change for nucleation ΔF_m is illustrated in Fig. 1. The parallel tangent construction is consistent with the formation of a nucleus whose composition is such that the *maximum* value of ΔF_m is obtained;¹⁴ hence this also represents the *most likely* composition of the nucleus, although such a criterion does not exclude the formation of nuclei of other compositions. The use of the nucleus composition corresponding to the maximum ΔF_m is a very good approximation for steels, since the solubility of carbon in ferrite is so limited that any carbon concentration up to the equilibrium level makes negligible difference to the magnitude of ΔF_m . Numerical values of ΔF_m can be obtained from the following equations, which may be readily derived from Fig. 1

$$\Delta F_{Fe}^{1-\alpha} + RT \ln \left[\frac{a_{Fe}^\alpha \{1-x\}}{a_{Fe}^\alpha \{1-\bar{x}\}} \right] - RT \ln \left[\frac{a_C^\alpha \{x\}}{a_C^\alpha \{\bar{x}\}} \right] = 0 \dots \dots (4)$$

$$\Delta F_m = RT \ln \left[\frac{a_C^\alpha \{x_m\}}{a_C^\alpha \{\bar{x}\}} \right] \dots \dots \dots (5)$$

where $a_{Fe}^\alpha \{1-x\}$ refers to the activity of iron in ferrite evaluated at the concentration $(1-x)$, and a similar rationale applies to the other activity terms. The term $\Delta F_{Fe}^{1-\alpha}$ refers to the free energy change accompanying the austenite-ferrite transformation in pure iron and R is the gas constant. The term \bar{x} is the average carbon concentration of the steel concerned and x_m represents the composition of ferrite which satisfies equation (4).

After iteratively solving equation (4), the ideal nucleus composition obtained is substituted into equation (5) to determine ΔF_m . The details of the calculations involved are given in Appendix 1. The analysis was confined to temperatures T_s below which it is thermodynamically possible to form a nucleus of the same substitutional alloying element content as the parent phase; this procedure is often used in the analysis of nucleation in steels^{1,15} and is satisfactory if the nucleus and parent phases are related by an atomic correspondence, as would appear to be the case for Widmanstätten ferrite and bainite,⁷ but is not necessarily correct for diffusional nucleation. However, if the analysis is confined to temperatures well below T_s , then it is likely that diffusional nucleation, like growth, also occurs without the partitioning of substitutional alloying elements. For the present purposes the assumption of no substitutional element partitioning considerably simplifies

Table 1 Results obtained by maximizing correlation coefficient

Activation enthalpy for diffusion $Q \times 10^{-6}$, J mol ⁻¹	Constant $-C_1 \times 10^{-2}$	Correlation coefficient R_1	Exponent p	C curve
0.0956	0.06030	0.85663	2	Shear
0.1104	0.01604	0.89339	3	Shear
0.2594	-0.42670	0.96285*	13	Shear
0.3427	0.36790	0.79653	2	Diffusional
0.4026	0.39640	0.84171	3	Diffusional
0.5224	0.45340	0.86801*	5	Diffusional

* Optimum values of R_1

the analysis, since a less extensive thermodynamic database is necessary to account for the multicomponent nature of the steels considered. Thus for alloy steels the first term of equation (4) is replaced¹⁶ by

$$[\Delta F_{Fe}^{\gamma-\alpha} \{T - 100 \sum Y_i \Delta T_{magi}\} + 141 \sum Y_i (\Delta T_{magi} - \Delta T_{nmi})]$$

where the terms within the curly brackets are to be interpreted as the arguments of the function $\Delta F_{Fe}^{\gamma-\alpha}$. The other terms are Y_i , the mole fraction of the i th substitutional alloying element, disregarding the presence of carbon, and ΔT_{magi} and ΔT_{nmi} , the displacements in the temperature at which the free energy change accompanying the austenite-ferrite transformation in pure iron is calculated, in order to account for the changes in the magnetic and non-magnetic components of $\Delta F_{Fe}^{\gamma-\alpha}$ respectively.

The experimental data of Ref. 17 were chosen for analysis because this is one of the more meticulously determined sets of TTT curves. Since the existence of two separable C curves is the basis of the analysis, only those diagrams¹⁸ whose component curves could be readily distinguished were used initially, although the results were subsequently applied indiscriminately. For diffusional transformations, the analysis was restricted to temperatures where $\Delta F^{\gamma-\gamma_1+\alpha} < -50$ J mol⁻¹ (where $\Delta F^{\gamma-\gamma_1+\alpha}$ represents the free energy change accompanying the growth of ferrite, without substitutional element partitioning; carbon partitioning during growth is taken into account) in order to increase confidence in the assumption that the only composition change occurring is that associated with the redistribution of carbon. Altering this arbitrary limit to -100 J mol⁻¹ did not significantly alter the results.

An inspection of experimentally determined TTT diagrams¹⁷ readily reveals the existence of a characteristic 'flat top' and a pronounced asymmetry in the shape of the shear transformation C curves. The flat top corresponds to the temperature at which the nucleation of displacive transformations first becomes possible.⁷ If this temperature also happens to be such that only a very limited amount of growth is possible (due to the 'incomplete reaction phenomenon'^{7,19}), then it is not meaningful to assign an 'incubation period' to this region of the TTT diagram since the transformation kinetics could be either nucleation or growth controlled. Hence only data 40 K below this region were chosen for analysis (other limits again did not

significantly alter the results). Furthermore, all data in the region of obvious overlap between the two component C curves were also rejected. Additionally, TTT curves (of Ref. 17) from incompletely austenitized steels were not included in the analysis. In this way a dataset of some 360 points was established for the purposes of detailed analysis.

RESULTS AND DISCUSSION

The results obtained by maximizing the correlation coefficient R_1 for equation (3) are listed in Table 1, which also includes data for $p = 2, 3$.

From these results it is evident that any of the values of p obtained could, within the limitations of the analysis, satisfactorily represent the experimental data in terms of equation (3), and that it is not justified to draw any fundamental conclusions from these results. Unfortunately, while high degrees of correlation have been obtained, the agreement was not found to be sufficiently good for the purposes of accurately predicting TTT diagrams. This is partly because the incubation time arises within a logarithmic term in equation (3), so that the amount of 'explained variation' in τ when converted into real time is less than that indicated by the correlation coefficients in Table 1. Hence an attempt was made to improve further the degree of correlation. It was noticed that the graph of $\ln [(\Delta F_m)^p \tau / T]$ against $1/RT$ exhibited systematic curvature and did not have the strict linear form implied by equation (3). This effect is consistent with the diffusion parameters, activation enthalpy and entropy, being temperature dependent, and (to a first order of approximation) can be better represented²⁰ as

$$Q = Q_0 + C_2(T - T_0) \dots \dots \dots (6)$$

$$S = S_0 + C_3 \ln(T - T_0) \dots \dots \dots (7)$$

where S, Q, C_2, C_3 , and T_0 are constants. Substituting into equation (2), we obtain

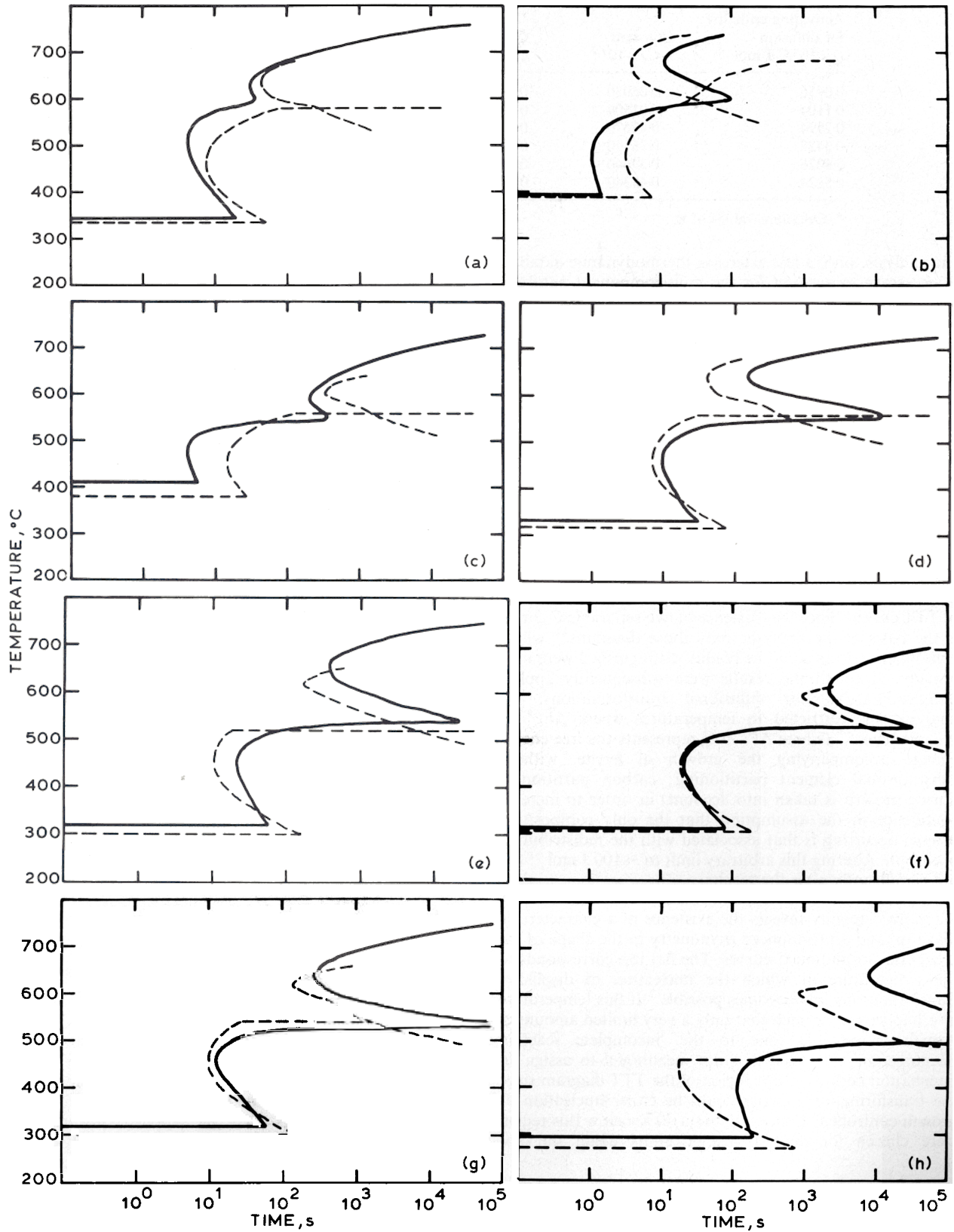
$$\ln \left| \frac{\tau (\Delta F_m)^p}{T^z} \right| = \frac{Q'}{RT} + C_4 \dots \dots \dots (8)$$

where z, Q' , and C_4 are constants. The results in Table 2 were then obtained using the modified equation.

Before these results can be applied towards the determination of TTT diagrams, certain further qualifi-

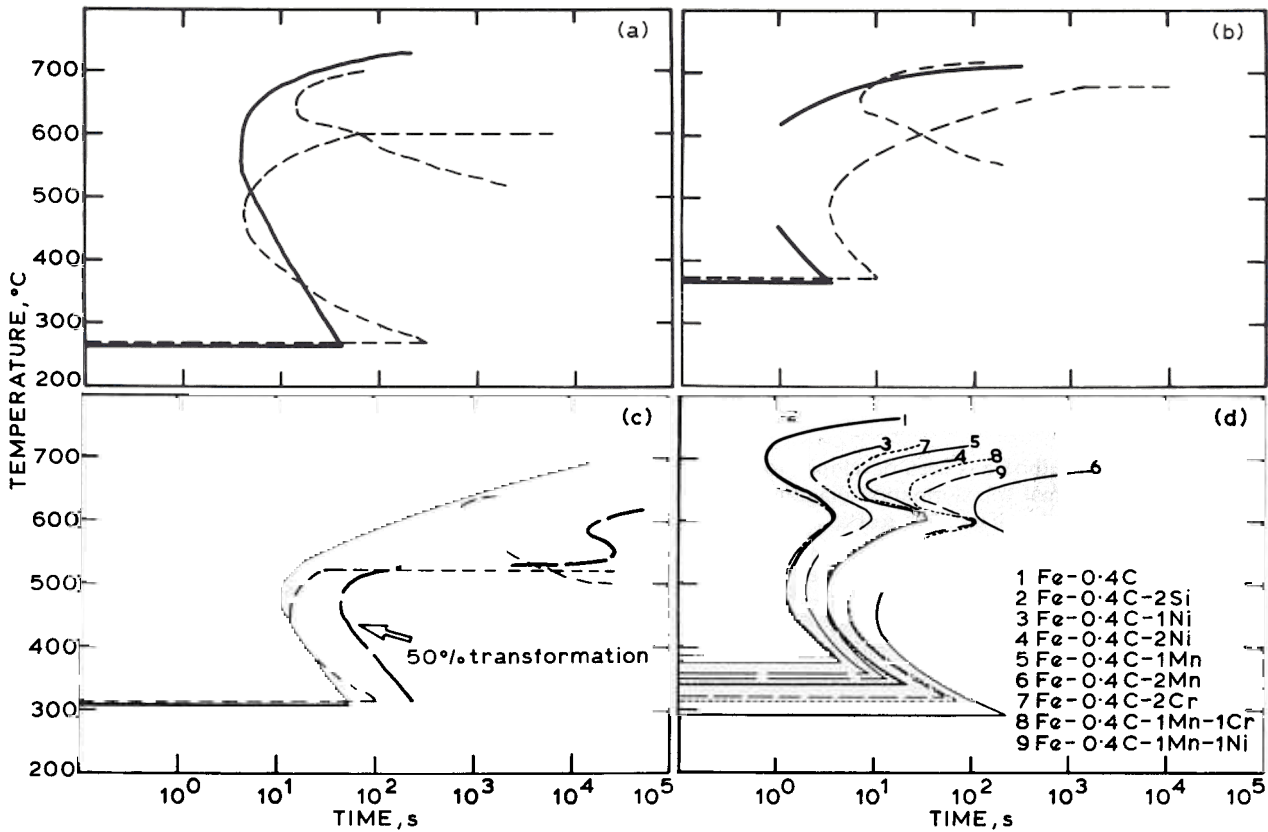
Table 2 Results obtained using modified equation

Constant $Q' \times 10^{-6}$ J mol ⁻¹	Constant $-C_4 \times 10^{-2}$	Correlation coefficient R_1	Exponent p	Constant z	C curve
0.2432	1.350	0.97428	5	20	Shear
0.6031	1.905	0.91165	4	20	Diffusional



a En 16; b En 20; c En 36; d En 17; e En 24; f En 23; g En 110; h En 26

2 Time-temperature-transformation diagrams showing degree of agreement between experimental¹⁷ and calculated (dashed lines) reaction-start curves; sequence also illustrates development of bay region for various steels



3 *a, b, and c* calculated (dashed lines) and experimental¹⁷ TTT diagrams illustrating discrepancies associated with study of low-alloy steels En 45, En 12, and En 21 respectively; *d* calculated TTT curves for series of hypothetical steels

cations are necessary. Bhadeshia⁷ has shown that the detectable nucleation of Widmanstätten ferrite and bainite requires $|\Delta F^{\gamma \rightarrow \gamma_1 + \alpha}|$ to exceed $|\Delta F_N|$, where, in formal accordance with isothermal martensite nucleation theory, ΔF_N is a linear function of temperature; this function can be adequately represented (see Appendix 2) by

$$\Delta F_N = 3.25175(T - 273) - 2183 \text{ J mol}^{-1} \dots (9)$$

Hence, above the temperature where $|\Delta F^{\gamma \rightarrow \gamma_1 + \alpha}| < |\Delta F_N|$, the incubation period for the shear transformation C curve can be effectively taken as infinite; the C curve can then be cut off by a horizontal line at this temperature, thus faithfully generating the experimentally observed flat top. A further precaution to be noted is that since the present analysis does not allow for substitutional element partitioning, the diffusional C curve should not be arbitrarily extrapolated to temperatures above which $\Delta F^{\gamma \rightarrow \gamma_1 + \alpha} > 0$. Finally, the relevant M_s temperatures may be calculated using the thermodynamic methods of Refs. 10 and 11.

A representative set of calculated and experimental (full lines) TTT diagrams is presented in Figs. 2 and 3, which are intended to reflect a wide range of steel compositions. Figure 2 illustrates the development of the bay region, from only a slight perturbation in an apparently continuous TTT curve (Fig. 2*a*) to a complete separation of the component shear and diffusional curves (Fig. 2*b*). The agreement is seen to be reasonable, particularly with respect to the relative movement of the component C curves; the correct prediction of this feature of TTT diagrams is important for hardenability evaluation and, when linked with the good fit

obtained in the bay region, provides a useful technique for theoretical steel design.

Space restrictions prevent the inclusion of more TTT diagrams, but the sort of agreement indicated in Fig. 2 was obtained for almost all of the steels of Ref. 17. Some discrepancies (Fig. 3) did arise in the case of very low-alloy steels where predicted cusps were not evident in the corresponding experimental reaction-start lines; however, the latter may have been incorrectly drawn since properly positioned cusps were evident, e.g. in the 50% transformation lines (Fig. 3*c*). In other cases it was obvious that the normal experimental techniques used in isothermal transformation work are not capable of achieving the high quench rates necessary to bypass the diffusional C curve in order to conduct tests in the bay region (Fig. 3). With the high reaction rates involved in these steels, careful and high-resolution tests would be necessary to detect any cusps.

Caution must be exercised in interpreting the detailed (calculated) shape of the bay region, since the analysis does not allow for the simultaneous occurrence of two different nucleation reactions. In such cases it is expected that the observed reaction-start time should be lower than that predicted on the basis of either of the component C curves, because the nucleation rates of the two reactions (at least at this very early stage of the transformation) should be additive. However, this effect would only be significant at, and in the immediate vicinity of, the point of intersection of the shear and diffusional C curves; otherwise, the contribution from one of the two reactions will be comparatively small, due to the near horizontal slope of the

C curves in this critical region. This means that the actual TTT diagrams should exhibit more rounded bays, rather than the very sharp calculated bays illustrated in Figs. 2 and 3.

As a matter of interest, Fig. 3d illustrates some predicted TTT diagrams for a number of hypothetical steel compositions; the alterations in shape of the respective TTT curves are in good accord with known effects of the various alloying elements on transformation kinetics.

Finally, it should be noted that the analysis does not allow for grain size variations, but it has been pointed out¹⁷ that such variations are small; in any case, unless site saturation occurs, the reaction-start times should not alter significantly with the usual range of austenite grain sizes obtained following commercial heat treatments.

CONCLUSIONS

A thermodynamic method has been developed to allow the prediction of isothermal transformation diagrams, starting simply from a knowledge of the chemical composition of the steel concerned. The accuracy obtained appears to be reasonable, and the technique is capable of correctly generating the bay region of time-temperature-transformation diagrams, while at the same time allowing relative shifts in the shear and diffusional C curves, as a function of alloying element content. However, it is clear that further quantitative work on nucleation and nucleation kinetics is necessary before any fundamental information can be obtained from an analysis of this type.

ACKNOWLEDGMENTS

The author is grateful to the Science Research Council for the provision of a research fellowship, and to Professor R. W. K. Honeycombe, FRS, for the provision of laboratory facilities. Valuable discussions with Professor Honeycombe are also acknowledged; his keen interest and encouragement throughout the course of this work are much appreciated.

REFERENCES

1. R. C. SHARMA and G. R. PURDY: *Metall. Trans.*, 1973, 4, 2303.
2. K. C. RUSSELL: *Acta Metall.*, 1968, 16, 761.
3. K. C. RUSSELL: *Acta Metall.*, 1969, 17, 1123.
4. J. S. KIRKALDY, B. A. THOMSON, and E. BAGANIS: 'Hardenability concepts with applications to steels', 82; 1978, Metals Park, Ohio, USA, American Society for Metals.
5. K. R. KINSMAN and H. I. AARONSON: 'Transformation and hardenability in steels', 39; 1967, Ann Arbor, Michigan, USA, Climax Molybdenum Co.
6. J. W. CHRISTIAN: 'Theory of transformations in metals and alloys', 673; 1965, Oxford, Pergamon.
7. H. K. D. H. BHADESHIA: *Acta Metall.*, 1981, 29, 1117.
8. C. L. MAGEE: 'Phase transformations', 115; 1970, Metals Park, Ohio, USA, American Society for Metals.
9. G. B. OLSON and M. COHEN: *Metall. Trans. A*, 1976, 7A, 1915.
10. H. K. D. H. BHADESHIA: *Met. Sci.*, 1981, 15, 175.
11. H. K. D. H. BHADESHIA: *Met. Sci.*, 1981, 15, 178.
12. J. W. CHRISTIAN: 'Theory of transformations in metals and alloys', Pt 1, 2 ed., 479; 1975, Oxford, Pergamon.
13. J. W. CHRISTIAN: 'Theory of transformations in metals and alloys', Pt 1, 2 ed., 375; 1975, Oxford, Pergamon.
14. M. HILLERT: *Acta Metall.*, 1953, 1, 764.
15. K. R. KINSMAN and H. I. AARONSON: *Metall. Trans.*, 1973, 4, 954.
16. H. I. AARONSON, H. A. DOMIAN, and G. M. POUND: *Trans. Met. Soc. AIME*, 1966, 236, 768.
17. BISRA, 'Atlas of isothermal transformation diagrams of B.S. En steels', Special report no. 56, 2 ed.; 1956, London, The Iron and Steel Institute.
18. BISRA, 'Atlas of isothermal transformation diagrams of B.S. En steels', Special report no. 56, 2 ed., 11, 17-27, 33, 37-45,

57, 59, 83, 95, 97, 107, 143, 151; 1956, London, The Iron and Steel Institute.

19. H. K. D. H. BHADESHIA and D. V. EDMONDS: *Acta Metall.*, 1980, 28, 1265.
20. N. L. PETERSON: 'Diffusion', 53; 1978, Metals Park, Ohio, USA, American Society for Metals.

APPENDIX 1

The thermodynamic methods used are based on the Lacher²¹ and Fowler and Guggenheim²² formalisms, as first applied to steels by Aaronson *et al.*^{16,23} This work was later corrected and reassessed by Shiflet *et al.*,²⁴ whose derivations are used throughout the present work but with the following modifications:

- (i) the equation giving the free energy for transformation from stress-free austenite to stress-free ferrite without any change in composition (i.e. the T_0 equation) has been modified as in Ref. 10 in order to allow for the high level of carbon in the supersaturated ferrite, and to account for Zener ordering
- (ii) in accordance with Refs. 25 and 26, the partial molar enthalpy $\Delta\bar{H}_y$ and the excess partial molar entropy $\Delta\bar{S}_y^{xs}$ of solution of carbon in austenite are taken to be functions of carbon content. The temperature dependence^{25,26} of $\Delta\bar{H}_x$ and $\Delta\bar{S}_x^{xs}$ is also taken into account.

Other thermodynamic data needed for the analysis are listed in Refs. 10, 11, 27, and 28. The Zener ordering energies were calculated as in Refs. 29 and 30. The influence of alloying elements was allowed for as in Refs. 11, 16, and 31. The ΔT_{mag} and ΔT_{nmi} were first derived by Zener, and are taken from Refs. 16 and 32. The influence of alloying elements of the carbon-carbon pairwise interaction energies in austenite can be obtained from Ref. 11. A FORTRAN IV computer program capable of doing all the necessary calculations (with an input of only the steel composition) is available on request.

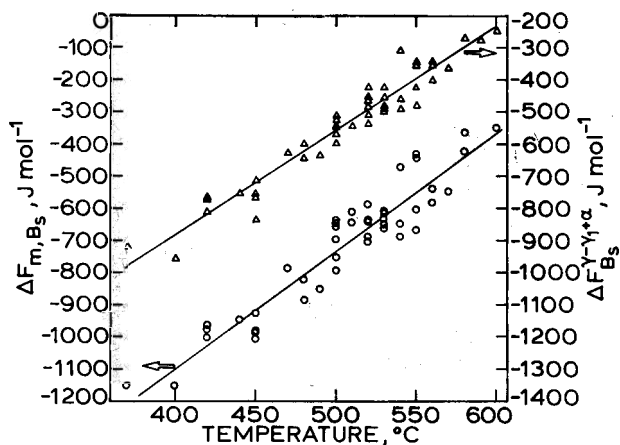
APPENDIX 2

A certain minimum amount of driving force ΔF_N is necessary before the onset of the nucleation of Widmanstätten ferrite and bainite.⁷ Furthermore, the nucleation of these phases seems to involve the equilibrium partitioning of carbon, and the criterion for nucleation can be expressed⁷ as

$$|\Delta F^{F-\gamma+\alpha}| > |\Delta F_N|$$

The function ΔF_N has been determined⁷ using the experimental data of Steven and Haynes,³³ but, in evaluating $\Delta F^{F-\gamma+\alpha}$, Bhadeshia, following Shiflet *et al.*,²⁴ did not take proper account of the variation of $\Delta\bar{H}_y$ and $\Delta\bar{S}_y^{xs}$ with carbon content (see Appendix 1). Although this leads to only a small error, it was felt necessary to redetermine ΔF_N in order to maintain a high level of internal consistency in the thermodynamic calculations; the methods and data involved in such calculations have been detailed elsewhere,⁷ but the new results are reported in Fig. 4.

The term $\Delta F^{F-\gamma+\alpha}$ allows for the change in austenite composition that accompanies the formation of ferrite. However, for nucleation this change will almost always be negligible due to the small volume of ferrite involved, and the chemical free energy change for this process would be better represented by ΔF_m (Ref. 14). The resulting alternative criterion for nucleation would make no difference to the calculated temperature at which nucleation first becomes possible, so long as the method of free energy



4 Diagram showing free energy available at so-called B_s temperature

calculation is clearly recognized. However, it was felt necessary to ensure that ΔF_N remains linear with temperature, as required by isothermal martensitic nucleation theory. The results are plotted in Fig. 4 and it is clear that linearity is indeed maintained.

It should be realized that the above results can as yet only be taken to be valid over the temperature range indicated in Fig. 4, and it is likely that at higher temperatures Widmanstätten ferrite nucleates from extant allotriomorphic ferrite, rather than directly from austenite grain boundaries.

REFERENCES

21. J. R. LACHER: *Proc. Cambridge Philos. Soc.*, 1937, **33**, 518.
22. R. H. FOWLER and E. A. GUGGENHEIM: 'Statistical thermodynamics', 1939, New York, Cambridge University Press.
23. H. I. AARONSON, H. A. DOMIAN, and G. M. POUND: *Trans. Met. Soc. AIME*, 1966, **236**, 753.
24. G. J. SHIFLET, J. R. BRADLEY, and H. I. AARONSON: *Metall. Trans. A*, 1978, **9A**, 997.
25. J. A. LOBO and G. H. GEIGER: *Metall. Trans. A*, 1976, **7A**, 1347.
26. J. A. LOBO and G. H. GEIGER: *Metall. Trans. A*, 1976, **7A**, 1359.
27. H. K. D. H. BHADOSHIA: *Met. Sci.*, 1980, **14**, 230.
28. L. KAUFMAN, E. V. CLOUGHERTY, and R. J. WEISS: *Acta Metall.*, 1963, **11**, 323.
29. J. C. FISHER: *Met. Trans.*, 1949, **185**, 688.
30. C. ZENER: *Trans. Met. Soc. AIME*, 1946, **167**, 550.
31. K. R. KINSMAN and H. I. AARONSON: 'Transformation and hardenability in steels', 15; 1967, Ann Arbor, Michigan, USA, Climax Molybdenum Co.
32. C. ZENER: *Trans. AIME*, 1955, **203**, 619.
33. W. STEVEN and A. G. HAYNES: *J. Iron Steel Inst.*, 1956, **183**, 349.

Proceedings of the international conference organized jointly by The Metals Society, London, and the Verein 'Eisenhütte Österreich', Leoben, and held at the Montanuniversität, Leoben, on 21–24 April 1980. The world's iron and steel industry has been deeply affected by the continuing energy crisis, owing in part to its position as one of the largest energy consumers. This conference looks at the achievements of the industry and the possibilities still open to it as it confronts the problems posed by radical changes in the cost and availability of energy.

The first session reviews the world energy scene and then examines its impact upon the industry and the responses available to steelmakers. Other sessions deal with relevant technical advances in ironmaking, steelmaking and hot working and highlight areas in which significant and cost-effective improvements can be made or where research should be undertaken.

Discussion periods, mainly in the form of written contributions, are also recorded in detail.

Metals Society Book 270 (ISBN 0 904357 32 5), published Spring 1981; 184 pages A4 (297 x 210 mm) casebound.

Prices: post-free to UK address £35.00 (Society Members £28.00); to Europe or overseas US\$90.00 (Members \$72.00). Please order, sending correct remittance and quoting book number 270, from

Book Sales Department, The Metals Society,
1 Carlton House Terrace, London SW1Y 5DB

[01-839 4071]

ENERGY-CONSCIOUS iron- and steelmaking

Book 270

