BAINITE : OVERALL TRANSFORMATION KINETICS

H.K.D.H. Bhadeshia

University of Cambridge, Department of Metallurgy and Materials Science, Pembroke Street, Cambridge, U.K.

Abstract. – New experimental results on the overall transformation kinetics of the bainite reaction (in three different steels) are interpreted in terms of recent work on the transformation mechanism of bainite. The analysis is shown to be consistent with (a) a linear dependence of the activation energy for isothermal nucleation, on the transformation free energy change, (b) the sub-unit mechanism of bainitic transformation, (c) the variation of nucleation rate with the degree of transformation, (d) hard and soft impingement effects and (e) alloying element effects. It is also suggested that the more conventional methods of analysing the overall transformation kinetics are inconsistent with the experimental results, and with the need to understand alloying element effects.

Introduction. – The relationship between the fraction of austenite transformed to bainite, and the time at constant temperature and alloy composition has never been evaluated in a manner consistent with the mechanism of the bainite transformation (1-4). Essential features of the transformation, such as the "incomplete-reaction phenomenon" (which has been shown to be a crucial feature of the bainite reaction Refs.5-8) cannot therefore be predicted, and similar difficulties arise in understanding the influence of substitutional alloying elements on the overall progress of the transformation.

This work is aimed at the interpretation of new experiments on the overall transformation kinetics of the bainite reaction, in terms of recent studies (5-8) on the transformation mechanism involved. Steels containing about 2 wt.pct. of silicon as an alloying element were used; these can be isothermally transformed to just bainitic-ferrite and residual austenite (9), the formation of carbides being completely suppressed. Hence, the kinetic measurements relate directly to the displacive formation of bainitic-ferrite, without intereference from any of the additional, diffusional reactions (such as carbide precipitation) which accompany the formation of bainite in conventional steels.

Experimental Procedures. – Two of the alloys used were made from high-purity constituents (5,8), with compositions Fe-0.39C-2.05Si-4.08Ni and Fe-0.22C-2.03Si-3.0Mn (wt.pct.); the third alloy (300M steel), obtained from Firth-Brown, had the composition Fe-0.44C-1.74Si-0.67Mn-1.85Ni-0.83Cr-0.39Mo-0.09V. The alloys were all homogenised at 1300°C for 3 days, either in a vacuum furnace or while sealed in quartz capsules containing pure argon. Specimens for dilatometric analysis were machined in the form of 3.2mm outer diameter cylinderical rods with a 1.5mm diameter bore and a 20mm length. They were then electroplated with a 0.075mm thick layer of Ni, essentially to provide

constraint and to eliminate surface degradation during heat treatment. After austenitisation in an atmosphere of pure helium (carried out in a Theta Industries high-speed dilatometer) at 1000°C for 5 mins, the specimen chamber was evacuated to facilitate the quench to the isothermal transformation temperature, by means of a controlled high-pressure He jet directed both radially and axially at the specimen, giving quench rates averaging $250-300°Cs^{-1}$. The length transducer on the dilatometer was calibrated by measuring the expansion coefficients of pure Ni and pure Pt rods. The linear expansivities of the ferrite and austenite (e_α, e_γ respectively) were measured over the temperature ranges 25-600°C and 800-990°C respectively, at heating or cooling rates of $5°C min^{-1}$. They were found to be constant over the temperature ranges studied. To determine e_α, specimens were first annealed at 600°C for 2 hrs before testing, in order to induce the thermal decomposition of any austenite; these measurements do not take account of the very small volume fraction of carbides present in the specimens. It is also assumed that e_γ is not a function of γ carbon content (x_γ), consistent with Ref.11. Lattice parameter measurements (using CoK_α radiation) were carried out using a Debye-Scherrer method, on heat-treated specimens which were chemically polished and thinned before testing. A Newton-Ralphson extrapolation, using $011,002,112,022_\alpha$ lines, was used to obtain the ambient temperature ferrite lattice parameter ($\bar{a}_\alpha$).

Since the accomodation factor of bainite sub-units can be shown to be nearly zero, the length change per unit length (i.e., $\Delta l/l$) corresponding to a volume fraction V of bainitic-ferrite is given by

$$\Delta l/l = (2Va_\alpha^3 + (1 - V)a_\gamma^3 - \bar{a}_\gamma^3)/(3\bar{a}_\gamma^3) \qquad \text{... (1)}$$

where $a_\alpha = \bar{a}_\alpha (1 + e_\alpha(T - 298))$, $\bar{a}_\gamma$ = lattice parameter of austenite with the mean alloy composition (at T) so that $\bar{a}_\gamma = (a_o + \Sigma c_i x_i)(1 + e_\gamma(T - 298))$, the c_i are coefficients relating alloying element concentration (x_i) to the change in the lattice parameter of unalloyed austenite (a_0). c_i were obtained from (11). Hence (12), (i=1≡Carbon)

$a_\gamma = (a_0 + c_1((\bar{x} - Vs)/(1 - V)) + c_i x_i)(1 + e_\gamma(T - 298))$,

where s = amount of carbon which remains in the ferrite (0.03 wt.pct., Ref.6) after transformation, and $\bar{x}$ is the mean carbon level of the alloy in wt.pct.

After making the appropriate substitutions, Eqn.1 can be solved to give V as a function of $\Delta l/l$. The experimental values of linear expansion coefficients and lattice parameters are given below.

	Fe-Mn-Si-C	Fe-Ni-Si-C	300M
$e_\alpha/°C^{-1}$	0.000013049	0.000011826	0.000011103
$e_\gamma/°C^{-1}$	0.000021151	0.000018431	0.000017951
$\bar{a}_\alpha/$Angstroms	2.8669∓0.002	2.8650∓0.0016	2.8661∓0.0010

Results and Discussion. - The experimental data are presented in Fig.1, plotted to be consistent with the form of a Johnson-Mehl-Avrami (13) equation,

$$\xi = 1 - exp(-kt^n) \qquad \text{...(2)}$$

so that the slope of each plot yields 'n', the intercept on the abscissa being 'ln(k)'. The time (t) corresponds to the number of seconds spent by the specimen at the isothermal transformation temperature, and $\xi = V/\theta$, where θ is the maximum volume fraction of bainitic transformation that can be achieved at a particular isothermal transformation temperature. It is evident (Fig.1) that the experimental data does not obey Eqn.2 for $\xi > 0.6$, and that there is no unique value of n (Fig.2) which can describe all the data. For an arbitrary, fixed value of ξ, a plot of ln(t) versus (1/nRT) is expected to yield an 'activation energy' (13), but detailed analysis indicated that ln(t) correlated very badly (linear correlation coefficients from -0.2 to 0.2) against (1/nRT). More significantly, if each of the lines of Fig.1 is claimed to be consistent

with Eqn.2, then it necessarily follows that the activation energy obtained must be independent of ξ. However, because of the considerable scatter in n, any activation energy deduced as discussed earlier, must <u>vary</u> with the (arbitrarily chosen) value of ξ for analysis. Hence, even if any particular set of isothermal data can perhaps be assessed to be consistent with Eqn.2, the total data set is clearly badly represented. Other methods of analysis (14, Eqn.4.9 of Ref.15, after correcting sign error) were also empirically applied, but without success, and a <u>mechanism</u> based theory was therefore initiated.

Recent work (5-9) indicates that the bainite transformation is diffusionless, growth of a 'sheaf' occurring by the martensitic propagation of 'sub-units' whose size is limited (to say a constant volume per sub-unit, 'v') by the build up of an accumulating friction stress which opposes and eventually terminates the growth of the sub-unit. The redistribution of carbon from these units of transformation (into the residual austenite) occurs <u>after</u> the actual transformation event, and a detailed thermodynamic analysis (6,8) has shown that the maximum permissible degree of transformation to bainitic ferrite (at T) is (approximately, since we ignore stored energy terms) given by

$$\theta = (x_{T_O} - \bar{x})/(x_{T_O} - s)$$

where x_{T_O} is the carbon level at which austenite and ferrite of identical composition have equal free energies.

In addition, it seems that the nucleation behaviour of both Widmanstätten ferrite and bainite is consistent with isothermal martensite nucleation theory (5), so that the activation energy for nucleation is a linear function of the chemical free energy change involved (ΔF_m, as discussed in Refs.16,17). The nucleation rate per unit volume, I, is given by

$$I = C_1 \exp\{-(C_2 + C_3\Delta F_m)/(RT)\} \qquad \ldots(3)$$

where C_2 and C_3 are constants.

If the nucleation rate at the Widmanstätten ferrite start temperature (Ws) is given by I_{Ws}, then Eqn.3 may be written as

$$I = I_{Ws}\exp\{(-(C_2 \Delta T)/(RTWs))-(C_3/R)((\Delta F_m/T)-(\Delta F_N/Ws))\} \qquad \ldots(4)$$

where $\Delta T = T - Ws$ and ΔF_N is given in Refs.5,16. The variation of ΔF_m with the amount of bainitic ferrite is taken to be

$$\Delta F_m = \Delta F_m^o\{1 - (C_4/C_3)\xi\theta\} \qquad \ldots(5)$$

and if $RT\Gamma = C_4\theta\Delta F_m^o$ then

$$\Delta F_m = \Delta F_m^o\{1 - ((\Gamma RT\xi)/(C_3 \Delta F_m^o))\} \qquad \ldots(6)$$

where ΔF_m^o is the free energy change for nucleation when $\xi = 0$, and C_4 and Γ are factors designed to reduce the driving force for nucleation as ξ increases. To account for autocatalytic effects (18), I_{Ws} may be further expanded as

$$I_{Ws} = I_o(1 + \beta\xi\theta) \qquad \ldots(7)$$

Using the 'extended volume' arguments of Avrami (see Ref.13), we may derive the additional relation (see Eqn. 58.4 of Ref.13)

$$\int(d\xi)/(I(1 - \xi)) = \int(vd\tau)/\theta \qquad \ldots(8)$$

where τ = the induction time at which a region nucleates. Hence,

$$\int_o(d\xi)/\{(1 - \xi)(1 + \beta\xi\theta)(\exp(\Gamma\xi))\} = \int_{\tau=o}^{t}(vI_o/\theta)d\tau \qquad \ldots(9)$$

On integrating Eqn.9, we get

$$\ln\{-A\ln(1 - \xi) + (B/(\beta\theta))\ln(1 + \beta\xi\theta) - (C/\Gamma)(\exp(-\Gamma\xi) - 1)\} - \ln(t/\theta) =$$
$$\ln(vI_o) - [(C_2 \Delta T)/(RTWs)] - (C_3/R)[(\Delta F_m^o/T) - (\Delta F_N/Ws)] \qquad \ldots(10)$$

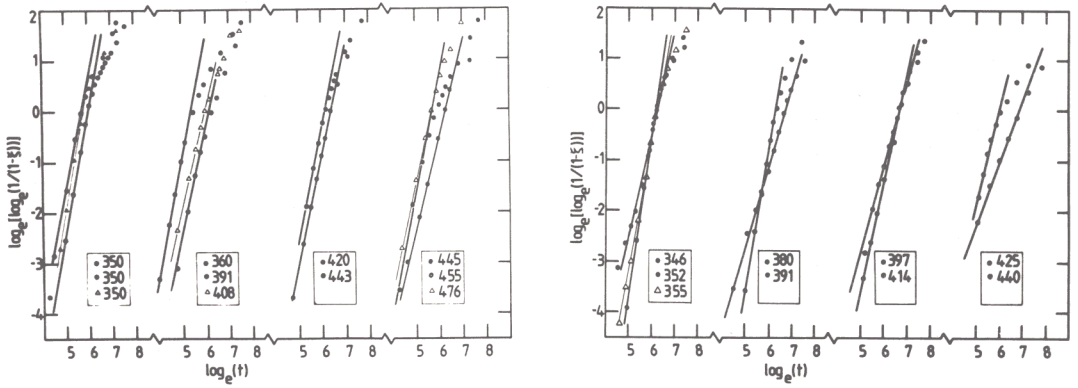where $A = (\exp(-\Gamma))/(1 + \beta\theta)$

Figure 1 Avrami plots of experimental data.
a) Fe-Ni-Si-C ,(b) Fe-Mn-Si-C , (c) 300M
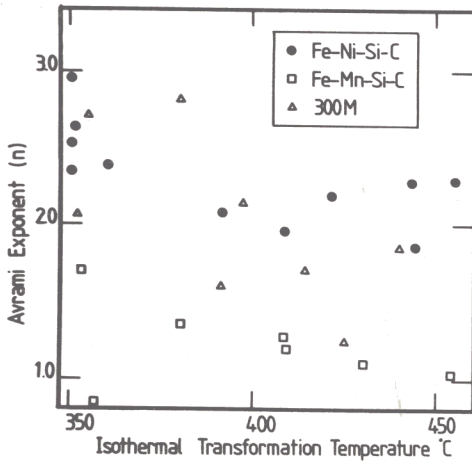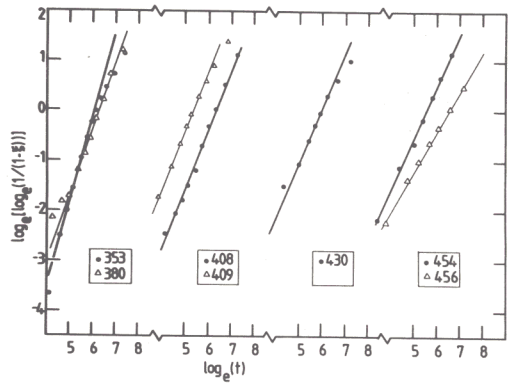The insets indicate the temperature (°C) of
transformation.

Figure 2
(a) Variation of n with T.

(b) Variation of ln(k) with (1/nRT)

$$C=[1-(\exp(\Gamma/\beta))(1-(1/\beta)+(A/\beta)+A\theta)]/[(1-(1/\beta))(1+\theta-(\exp(\Gamma/\beta)))]$$
$$B=1-A-C$$

The left hand side of Eqn.10 is henceforth referred to as 'δ'.

For an isothermal experiment, Eqn.10 indicates that δ should have a fixed value, independent of ξ or t. This provides an <u>independent</u> method of solving for β and C_4, since the latter have to be chosen to satisfy this condition. Hence, β was found to be 200, and $C_4=11$, giving variations in δ of less than 10% for any individual isothermal experiment. Multiple regression analysis, which included a routine for testing the fit between the calculated and experimental times (for any value of ξ, for all the data), was used to obtain $C_3=3.769$ (dimensionless) and $C_2=29710$ J/mol, with $\ln(vI_o)= -9$. It is interesting that the last term implies that there exists an extremely small nucleation rate at Ws (i.e., the highest temperature of the 'shear' C curve – see Ref.16) consistent with the interpretation of Time–Temperature–Transformation curves given in (5). C_2 and C_3 are about an order of magnitude smaller than those associated with low–temperature isothermal martensite kinetics (19), and the reasons for this are not clear; nevertheless, the reasonable degree of agreement between the experimentally measured times for transformation to various values of ξ, and the time calculated via Eqn.10 for the same values of ξ is illustrated in Fig.3. It should also be noted that the small value of β is consistent with the fact that bursts of bainitic transformation do not occur.

Despite the extensive computing carried out to establish the above constants, it is not clear that optimum values have been reached. Some of the scatter in Fig.3 can be attributed to the fact (Fig.1) that experiments repeated under identical conditions give significantly different results. However, it is also evident that the analysis based on Eqn.10 does not fully account for "second order" (Fig.3) alloying element effects, since the three alloys exhibit different scatter about the line of unit slope in Fig.3. The calculations also indicated a small but systematic tendency to overestimate the reaction rates at higher temperatures.

<u>Conclusions.</u> – A mechanism based theory for the overall transformation kinetics of the bainite reaction has been developed, which gives good overall agreement with experimental data, although further work is considered necessary to properly account for certain systematic errors in prediction.
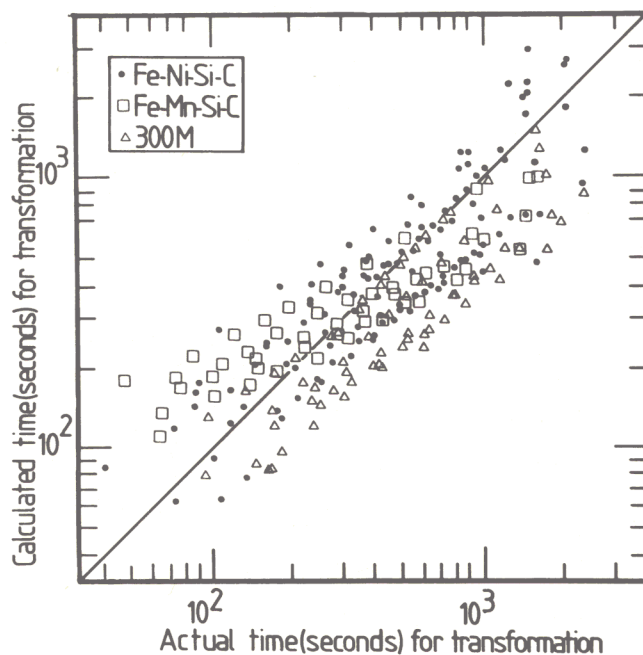
Figure 3 Comparison of calculated and experimentally measured times for various degrees of isothermal transformation.

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