TIME-TEMPERATURE-TRANSFORMATION DIAGRAM within the BAINITIC TEMPERATURE RANGE in a MEDIUM CARBON STEEL

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Synopsis

The time-temperature-transformation (TTT) diagram within the medium temperature range of medium carbon steel has been determined. A single type of C-curve is found within the bainite temperature range for the studied steel. Distinct reaction C-curves were not observed for both types of microstructure, upper bainite and lower bainite in the TTT diagram. Experimental results on the kinetics of the isothermal formation of bainite at different temperature have demonstrated that both type of microstructure, upper and lower bainite, possesses similar overall transformation kinetics. Some applications of phase transformation theory towards the formation of bainitic microstructures are discussed, with particular emphasis on the

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bainite start temperature, transition temperature from upper to lower bainite, martensite start temperature and the thickness of bainitic plates.

Abridged title: ISOTHERMAL BAINITE FORMATION in a MEDIUM-CARBON STEEL

1. Introduction

Bainite can be regarded as a non-lamellar mixture of ferrite and carbides, but within this broad description, it is possible to identify two classical morphologies, traditionally named upper and lower bainite. Both upper and lower bainite consist of plates of ferrite, known as sub-units, separated by cementite. The plates of ferrite grow in aggregates called sheaves of bainite. Within each sheaf, the plates of ferrite are parallel and share a common crystallographic orientation. The essential difference between upper and lower bainite is with respect to the carbide precipitation. In upper bainite, the bainitic ferrite is free of precipitation; carbides grow from the regions of carbon enriched austenite, which are trapped between the sub-units of ferrite. By contrast lower bainitic ferrite contains a fine dispersion of plate-like carbides within the bainitic ferrite plates.

Both upper and lower bainite are formed by the propagation of displacive ferrite sub-units followed by the partition of the excess carbon into the residual austenite. Cementite can then precipitate from the enriched austenite between the ferrite plates. The growth of the bainitic sub-units is accompanied by a change in the shape of the transformed region, which can be described as an invariant-plane strain with a large shear component. The parent austenite cannot accommodate the large shape deformation elastically and relaxes by plastic deformation in the region adjacent to the bainite. This plastic deformation stifles the growth of bainite sub-units before they hit any

obstacle, and the transformation proceeds with the formation of a new sub-unit [1]. The mechanism of transformation continues until the carbon concentration of the residual austenite reach the T_o curve, at which ferrite and austenite with identical chemical composition have the same free energy [2-5] (or $T_o^{'}$ curve, if the strain energy due to the displacements associated with the transformation is considered).

In lower bainite formation, the slower diffusion associated with the reduced transformation temperature provides an opportunity for some of the carbon to precipitate in the supersaturated bainitic ferrite. A fine dispersion of plate-like carbides is then found inside the ferrite plates [6], with a single crystallographic variant within a given ferrite plate [7] although it is possible to observe more than one variant of carbide precipitation in a lower bainite sub-unit [8].

Takahashi and Bhadeshia [9] developed a model to estimate the transition temperature from upper to lower bainite based on the hypothesis that bainitic ferrite grows with a supersaturation of carbon in solid solution. In this model the lower bainite start temperature (LB_s) is calculated comparing the time required to decarburise supersaturated ferrite and the time required obtaining a detectable degree of cementite precipitation in the bainitic ferrite. Thus, the time required to decarburise a supersaturated bainitic ferrite plate of thickness w is given by,

$$t_d = \frac{w^2 \left(\bar{x} - x^{\alpha\gamma} \right)^2}{16 \overline{D} \left(x^{\gamma\alpha} - \bar{x} \right)^2} \tag{1}$$

where $\bar{x}$ is the average carbon concentration in the steel as a whole, $x^{\alpha\gamma}$ and $x^{\gamma\alpha}$ are the carbon concentrations in ferrite and austenite, respectively, when both phases are in paraequilibrium, and $\bar{D}$ is the weighted average diffusivity of carbon in austenite. Likewise, the time interval t_θ necessary to obtain an amount of cementite precipitation in the ferrite can be determined from the Avrami relationship, which expresses the change in volume fraction of cementite precipitation as a function of time and temperature. The parameters of this relationship were calculated from tempering experimental data of plain carbon steels [9].

The bainite reaction has its own C-curve centred between the pearlite and the martensite ranges on a time-temperature-transformation (TTT) diagram, whether upper bainite and lower bainite have the same C-curve [10, 11] or their own C-curves [12] are not clear. Likewise, the displacive C-curve presents a characteristic flat top at a temperature T_h which is the highest temperature at which ferrite can form by displacive transformation [13].The transformation product at T_h can be Widmanstätten ferrite or bainite. If the driving force at T_h is sufficient to account for diffusionless growth, then T_h is identified with the bainite-start temperature (B_s) and Widmanstätten ferrite does not form at all. This theory provides a thermodynamic method for the calculation of B_s [2]. There also exist several empirical formulas for the prediction of B_s as a function of the chemical composition [14-17], which contain different alloying elements and ranges of use.

The martensite start temperature (M_s) generally features on a TTT diagram as a horizontal line parallel to the time axis as a lower limit to the bainite range. As occurs in the case of the B_s calculation, there are some empirical formulas for M_s as a function of the chemical composition [14, 18-23] with different grades of accuracy depending on the allowed range of alloying elements. An alternative approach is to use thermodynamic theory, which has the advantage that any solute combination can be considered on condition that the thermodynamic data are available. In the thermodynamic approach, martensite is said to be triggered when the free energy change accompanying the transformation of austenite to martensite of the same composition achieves some critical value at M_s. Ghosh and Olson [24] explicitly defined the critical driving force needed to start martensite formation in terms of solute concentration by using solid solution theory. The inputs of Ghosh and Olson's model are the chemical composition and the free energy change for the transformation of austenite to ferrite of the same composition, $\Delta G^{\gamma\alpha}$. More recently, Capdevila *et al.* [25-27] developed a model using artificial neural networks for the determination of M_s, including the effect of chemical composition and the prior austenite grain size (PAGS) in calculations.

In the present work, the partial TTT diagram within the bainitic temperature range of medium carbon steel has been determined. Experimental results on the kinetics of the isothermal formation of bainite at different temperatures have allowed studying separately the overall transformation kinetics of upper and lower bainite. Moreover,

some applications of phase transformation theory towards the formation of bainitic microstructures are discussed, with particular emphasis on the bainite start temperature, transition temperature from upper to lower bainite, martensite start temperature and the thickness of bainitic plates.

2. Materials and Experimental Procedures

The chemical composition of the studied steel is given in Table 1. The material was supplied as 30 mm hot rolled square bar. Dilatometric analysis and heat treatments were carried out using an Adamel Lhomargy DT1000 high-resolution dilatometer described elsewhere [28], The heating device consists of a very low thermal inertia radiation furnace. The power radiated by two tungsten filament lamps is focussed on the specimen by means of a bi-elliptical reflector. The temperature is measured with a 0.1 mm diameter Chromel-Alumel (Type K) thermocouple welded to the specimen. Cooling is performed by blowing a jet of helium gas directly onto the specimen surface. These devices ensure an excellent efficiency in controlling the temperature and holding time of isothermal treatments and as well as fast cooling in quenching processes.

Cylindrical dilatometric test pieces of 2 mm in diameter and 12 mm in length were austenitised for 60 seconds at 1200 ºC, and then isothermally transformed at temperatures ranging from 300 to 550 ºC for different times before quenching to room temperature. A simple

lever rule based on the consideration that there is no carbon enrichment of the austenite during transformation, which causes a variation of the lattice parameter of the austenite, allows us estimating the evolution of the volume fraction of bainite, V_b, with time from the recording of the change in length of the specimen during transformation,

$$V_b = V_b^{max} \cdot \frac{L(t) - L_o}{L_f - L_o} \qquad (2)$$

where V_b^{max} is the maximum volume fraction of bainite formed at the end of the isothermal reaction assessed by metallography, $L(t)$, L_o and L_f are the lengths of the specimen at t, before and after the completion of the transformation, respectively. This simple procedure was confirmed by comparing the bainite volume fraction assessed by metallography and dilatometry using eq. (2).

Optical and scanning electron microscopes (SEM) were used to examine the etched microstructures. Specimens were ground and polished using standard techniques and etched in 2% nital solution and examined using a Jeol JSM-6500F Field Emission Scanning Electron Microscope operating at 7 kV. The volume fraction of bainite was estimated by a systematic manual point-counting procedure on scanning electron micrographs [29]. A grid superimposed on the microstructure provides, after a suitable number of placements, an unbiased statistical estimate of V_b. Stereological errors for V_b values correspond to the standard deviation of the measurement. Moreover,

the true plate-thickness of bainitic ferrite, w, was estimated on scanning electron micrographs of fully transformed specimens by measuring the mean lineal intercept, $\overline{L}_T = \pi w / 2$, in a direction normal to the plate length. The thickness w can be also related to the mean lineal intercept measured using randomly oriented test lines by the relation $\overline{L} \approx 2w$ [30], but $\overline{L}_T$ is easier to measure since it is rare in scanning electron micrographs that entire plates of bainite can be imaged.

The M_s temperature of the steel was measured by dilatometry. Cylindrical specimens 12 mm in length and 2 mm in diameter were heated to 1200 ^{o}C and then rapidly cooled. Each dilatometric test was performed twice. The formation of martensite during cooling was detected by monitoring the fractional change in dilatation with temperature.

Vickers hardness tests were carried out on heat treated samples. The results correspond to the average of at least five tests.

Cylindrical samples 3 mm in diameter and 12 mm in length were used to reveal grain boundaries by the thermal etching method [31]. For this purpose, a surface 2 mm in width was generated along the longitudinal axis of samples by polishing and finishing with 1µm diamond paste. Later on, samples were austenitised in vacuum (>1Pa) at 1200 ºC for 60 seconds. Subsequently samples were cool down to room temperature at 1 ºC/s. These samples do not require metallographic preparation after heat treatment; the prior austenite grain boundaries

are revealed without chemical etching. The average austenite grain size was measured using an image analyser.

3. Results and Discussion

3.1. Determination of M_s, B_s and LB_s temperatures

The M_s temperature of the steel was measured by dilatometry monitoring the related change in dilatation with temperature. A value of M_s = 342 ºC was recorded on dilatometric curves. Figure 1 shows representative microstructures at relatively late stages of transformation at temperature just above and below the M_s temperature assessed by dilatometry. Micrographs suggest that martensite was formed at 340 ºC, whereas the microstructure obtained at 355 ºC consists of lower bainite. Likewise, an increase in hardness of 40 HV is detected when decomposition temperature decreases from 355 to 340 ºC. These results thus confirm the M_s temperature initially assessed by dilatometry.

Figure 2 shows optical and scanning electron micrographs of samples isothermally transformed at 550 ºC and 525 ºC. As decreasing decomposition temperature from 550 ºC to 525 ºC, microstructure markedly changes. At 550 ºC, austenite transforms into a mixture of proeutectoid ferrite and pearlite, whereas upper bainite consisting of ferrite laths forming in parallel becomes dominant at 525 ºC. The morphology of proeutectoid ferrite is not polygonal at 550 ºC, side-

plates in addition to allotriomorphs are observed at this temperature. On the other hand, as increasing time from 900 to 1800 s at 525 ℃ degenerated pearlite characterised by the polygonal gross microstructure involving non-lamellar carbide is seen together with upper bainite in the microstructure. However, the microstructure becomes fully bainitic and degenerate pearlite is not longer seen at temperatures below 500 ℃. All these metallographic results suggest that B_s temperature of the steel is around 525 ℃. As decreasing the decomposition temperature the carbide density in the bainitic microstructure becomes higher as shown in Figure 3. This figure shows microstructures formed at temperatures between 500 and 375 ℃ at relatively late stages of transformation.

There is no fundamental difference in transformation mechanism for upper and lower bainite [9]. The bainitic ferrite grows supersaturated with carbon. The excess carbon may then partition into the residual austenite or precipitate in the ferrite in the form of carbides. If the latter process is dominant, lower bainite is obtained. Upper bainite is obtained only when carbon partitions relatively rapidly into the residual austenite, before the carbides have an opportunity to precipitate. According to this model, it is also possible to form a mixed microstructure of upper and lower bainite in a narrow temperature range around LB_s temperature. This is because the carbon enrichment of the austenite caused by upper bainite transformation can result in a subsequent formation of lower bainite [9].

In the studied steel, upper bainite is formed at temperatures ranging from 525 ℃ to 475 ℃ (See Figures 2.d and 3.a-b), whereas lower bainite is present in microstructures formed at temperatures between 425 ℃ and 355 ℃ (See Figures 3.d-f and Figure 1.c). A mixed microstructure of both forms of bainite is observed at 450 ℃ as shown in Figure 3.c. It is noted that a lower bainite plate contains one major and some minor variants of carbides precipitates within bainitic ferrite in the right-hand side of the micrograph. However, in the left-hand side, upper bainite sheaves can be found. It can be then concluded that the transition from upper to lower bainite occurs at a temperature about 450 ℃.

Table 2 lists the M_s temperature of the studied steel calculated from different empirical formulas [14, 18-23], thermodynamic theory [24], and neural network analysis [25-27], in comparison with the M_s experimental value. The free energy change for the transformation of austenite to ferrite of the same composition, $\Delta G^{\gamma\alpha}$, input in Ghosh and Olson model [24] was calculated using MTDATA [32]. Likewise, the artificial neural network method [27] requires the PAGS as an input (39 μm in the studied steel). Calculated values in Table 2 suggest that thermodynamic theory and artificial neural network analysis are accurate methods to estimate M_s temperature. Likewise, empirical formula developed by Carapella, and Rowland and Lyle predict for the studied steel a value of M_s quite close to the experimental value.

On the other hand, Table 3 lists the B_s temperature of the studied steel calculated from different empirical formulas [14-15, 17], and bainite

theory [33]. If the process of bainite reaction is consider diffusionless, the highest temperature at which bainite can grow should be below the T_o line. The T_o concept was first introduced by Zener [13] and modified by Aaronson *et al.* [34, 35] A further calculation was carried out by Bhadeshia and Edmonds [36] allowing for the effect of elastic strain due to transformation, giving a strain energy of about 400 J mol^{-1} (T_o' line). A way of predicting B_s temperature is to introduce the universal nucleation function (G_N), which was determined experimentally by Ali and Bhadeshia [37], in addition to the growth criterion (T_o') described previously. Nucleation of bainite is possible only when the maximum free energy change accompanying the nucleation (G_M) is larger than G_N in absolute value. Thus, the B_s temperature for a given alloy can be predicted to be the lower value of its corresponding T_o' temperature and the temperature at which $|G_M| > |G_N|$. B_s calculated values in Table 3 suggest that Bhadeshia method based on bainite theory is an accurate method to estimate B_s temperature. In this case, all the empirical formulas tested fail in the prediction of B_s temperature.

Finally, Takahashi and Bhadeshia model [9] has been used to estimate the LB_S temperature of the studied steel. In this sense, the time required to decarburise supersaturated ferrite, t_d, and the necessary time to obtain a detectable amount of cementite precipitation in the ferrite, t_θ, as a function of decomposition temperature were calculated. There is no reliable method for the calculation of t_θ as a function of temperature. Here, data obtained by Takahashi and Bhadeshia [9] corresponding to a Fe-0.3 wt-%C plain carbon steel were used. On the

other hand, eq. (1) was used for the determination of t_d. In this equation, the diffusivity of carbon in austenite, $\overline{D}$, was calculated using Babu and Bhadeshia model [38], and the carbon concentrations in ferrite and austenite, $x^{\alpha\gamma}$ and $x^{\gamma\alpha}$, respectively, were determined using MTDATA in paraequilibrium conditions [32]. Likewise, the bainitic ferrite plate thickness, w, was measured for the studied steel at different transformation temperature on scanning electron micrographs. An average w value of 0.18 μm was estimated. Results of t_d along with t_θ values are shown in Figure 4.

Comparing both t_d and t_θ values, it can be concluded that the minimum temperature at which $t_\theta < t_d$ is, approximately, 370 ºC. This temperature would correspond to the transition temperature from upper to lower bainite. The calculated LB_s temperature is quite low in comparison to the experimental value, 450 ºC. A more precise determination of t_θ, including the influence of alloying elements in calculation, is indispensable for the estimation of LB_s temperature. Moreover, the reactions of partition of carbon into the residual austenite and the precipitation of carbides in the bainite should interact. Partitioning reduces the amount of carbon available for precipitation and vice versa. This effect should be taken into account in a more reliable theory for the transition from upper to lower bainite.

3.2. Scale of microstructure

In the absence of precipitation, the thickness of bainite plates depends primarily on the strength of the austenite at the transformation temperature, and the chemical free energy change accompanying transformation [39]. This applies specifically when the shape deformation causes plastic strain in the adjacent austenite. Strong austenite or a large driving force results in finer plates, the former because there is a larger resistance to interface motion and the latter because an increased nucleation rate leads to microstructural refinement. Temperature by itself does not have much of an effect. In this sense, Singh and Bhadeshia [40] developed a model using artificial neural network for the determination of the thickness of bainite plates, including the effect of temperature, austenite strength and driving force for nucleation of bainite. The validity range of temperature for the model is 260 ℃-460 ℃.

In order to find the role that cementite precipitation might play in the final thickness of bainitic plates, Singh and Bhadeshia model was used to calculate the thickness of bainite plates in the studied steel beside cementite precipitation occurs during bainite formation. The driving force for bainite nucleation was determined using thermodynamic theory [33] and the austenite strength was calculated using Young and Bhadeshia empirical model [41], where the yield strength of austenite is expressed as a function of the transformation temperature and the chemical composition of the alloy.

The measured plate thickness w is plotted as a function of transformation temperature in Figure 5 and compared with the results

of the model above described. Experimental error bars corresponds to the standard deviation on the thickness of ~ 400 bainite plates. Moreover, an average error of 0.03 μm can be considered for calculations according to Singh and Bhadeshia [40]. The model accurately fits the experimental results even out of its range of validity. As expected, *w* increases with the isothermal transformation temperature. Thus, results suggest that the origin of this trend is in the growth mechanisms of bainitic ferrite sub-units and is independent of carbide precipitation processes. There is a plastic relaxation in the austenite adjacent to the formed bainite plates and the dislocations generated resist the advance of the bainite/austenite interface, the resistance being greatest for strong austenite. As the yield strength of the austenite decreases with increasing temperatures, it is expected that the plates become thicker. Significant differences in this behaviour have not been detected between upper and lower bainite as Figure 5 shows.

Two main factors contribute to the hardness of a fully bainitic microstructure: the plate thickness of bainitic ferrite and the presence of cementite particles inside or between ferrite plates. Figure 6 shows the hardness of specimens fully transformed to bainite as a function of isothermal transformation temperature. As expected, the lower the transformation temperatures the higher the hardness of bainitic microstructure. This trend is explained by the decrease in the plate thickness of bainitic ferrite (Figure 5) and the increase in the density of carbides present in the microstructure. Results also suggest a

significant increase in hardness when transition from upper to lower bainite occurs due to the precipitation of finer carbides within bainitic ferrite plates.

3.3. Overall transformation kinetics

Isothermal kinetics for the studied steel in the temperature range 525-375 °C is presented in Figure 7. Close cycles in this figure correspond to the volume fraction of bainite measured by a systematic manual point-counting procedure on scanning electron micrographs, whereas solid line represent the evolution of the volume fraction of bainite with time determined from dilatometric curves using eq. (2). Both procedures essentially lead to the same results. Fully bainitic microstructures are obtained at all the tested temperature. Likewise, squares in Figure 7 represent the evolution of hardness as a function of time. Hardness decreases as bainite transformation proceeds since the volume fraction of martensite is reduced in the microstructure.

As an example of the evolution of the volume fraction of bainite with time, the optical micrographs corresponding to the isothermal treatments carried out at 375 °C are shown in Figure 8. After 3 s of holding time at this temperature, bainite transformation has not started and a fully martensitic microstructure is obtained by quenching (Figure 8.a). The first sheaves of bainite nucleated on prior austenite grain boundaries are observed after 6s of holding time (Figure 8.b). Figures 8.c-e show intermediate stages in the transformation.

Transformation is completed after 300 s of holding time when a fully bainitic microstructure is obtained (Figure 8.f).

The conventional Avrami equation is generally used to describe the overall transformation kinetics under isothermal conditions:

$$\xi = 1 - \exp\{-bt^n\} \tag{3}$$

where ξ is the volume fraction of austenite transformed within holding time t, n is the Avrami exponent indicative of the transformation mechanism, and b is a temperature dependent factor. Eq.(3) can be rewritten as:

$$\ln\left[\ln\left(\frac{1}{1-\xi}\right)\right] = n\ln t + \ln b \tag{4}$$

Therefore the value of n at the different tested temperatures is given by the slope of $\ln[\ln(1/1-\xi)]$ *vs.* $\ln t$ plots of the overall transformation data shown in Figure 7. In this analysis, the data were limited to those having a value of $\ln[\ln(1/1-\xi)]$ less than zero, that is $\xi<0.6$, where linearity between $\ln[\ln(1/1-\xi)]$ and $\ln t$ is well preserved [42]. Figure 9 represents the values of n as a function of the transformation temperature. It is clear that isothermal kinetics exhibit a constant Avrami exponent close to 2 in the whole investigated range. This value indicates that bainitic reaction can be described by a linear growth of ferrite plates nucleated at austenite grain surfaces with a constant rate [43]. Growth is indeed considered to occur mainly in one dimension assuming that thickening of the plates can be neglected

compared to their lengthening. Differences in the n values corresponding to upper and lower bainite have not been found.

About the temperature dependence of the isothermal bainite transformation rate, it has been reported [44] that there exists an overall activation kinetics given by:

$$Q_\xi^* = R\left[\frac{\partial \ln t}{\partial(1/T)}\right]_\xi \tag{5}$$

where t is the time to reach a certain transformed fraction ξ, T is the isothermal holding temperature and R is the gas constant. The term ξ is usually taken as 0.5 in most literature [12] and the value of $Q_{0.5}^*$ is calculated with the slope of the straight line $\ln t$ $vs.$ $1/T$. Table 4 lists $Q_{0.5}^*$ values determined for upper and lower bainite in the studied steel. Overall kinetics data at 450 ºC were not considered in the calculations since a mixed microstructure was obtained at this temperature. Similar $Q_{0.5}^*$ values for upper and lower bainite were found, but lower than those reported elsewhere [12, 44]. This might indicated that the rate of overall transformation in the steel studied is higher. It is clear from n and $Q_{0.5}^*$ results (Figure 9 and Table 4) that upper and lower bainite present similar overall transformation kinetics.

Figure 10 shows the 5 and 50 % bainite TTT curves determined by dilatometry for the studied steel. Solid lines in this graph mark the tendency of experimental values (circles symbols) for the bainite curves taking into account the error in time associated to the determination of the volume fraction of bainite using dilatometric

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analysis (dashed lines). By contrast to previous reports [8, 45], TTT curves appear to exhibit a single C-curve within the bainite temperature range for the studied steel for the upper and lower bainite. Distinct reaction C-curves were not clearly observed for both types of microstructure, upper bainite and lower bainite in the TTT diagram. This is consistent with n and $Q_{0.5}^*$ results found for upper and lower bainite. A significant acceleration of lower bainite overall transformation kinetics near the LB_s temperature compared with upper bainite formed just above LB_s temperature is not observed. However, transformation curves indicate that there may be a slight acceleration of transformation to lower bainite as M_s temperature is approached [8].

4. Conclusions

A single type of C-curve has been found in the TTT diagram within the bainite temperature range for the studied steel. Distinct reaction C-curves were not observed for both types of microstructure, upper bainite and lower bainite in the TTT diagram. Experimental results on the kinetics of the isothermal formation of bainite at different temperature have demonstrated that both type of microstructure, upper and lower bainite, possesses similar overall transformation kinetics. Finally, it has been shown that phase transformation theory can be used to calculate with a very good agreement the martensite and bainite start temperatures, and the thickness of bainitic ferrite plates, but a more precise determination of the transition temperature from upper to lower bainite is required.

5. Acknowledgement

6. References

1) H. K. D. H. Bhadeshia and J. W. Christian: Metall. Trans. A, **21** (1990) 767-97.

2) H. K. D. H. Bhadeshia: Acta Metall. **29** (1981) 1117-1130.

3) H. K. D. H. Bhadeshia and A. R. Waugh: Acta Metall. **30** (1982) 775-784.

4) L. C. Chang and H. K. D. H. Bhadeshia: Mater. Sci. Eng. A **184** (1994) L17-L20.

5) I. Stark, G. D. W. Smith and H. K. D. H. Bhadeshia: *Solid→Solid Phase Transformations*, ed. by G. W. Lorimer (Institute of Metals, London, 1988) pp. 211-215.

6) S. J. Matas and R. F. Hehemann: Trans. Met. Soc. AIME **221** (1961) 179-185.

7) H. K. D. H. Bhadeshia. Acta Metall. **28** (1980) 1103-1114.

8) L. C. Chang: Mat. Sci. Eng. A **368** (2004) 175-182.

9) M. Takahashi and H. K. D. H. Bhadeshia: Mater. Sci. Technol. **6** (1990) 592-603.

10) B. L. Bramfitt and J. G. Speer: Metall. Trans. A **21** (1990) 817-829.

11) H. Ohtani, S. Okaguchi, Y. Fujishiro and Y. Ohmori: Metall. Trans. A **21** (1990) 877-888.

12) M. K. Kang, D. M. Chen, S. P. Yang and G. L. Hu: Metall. Trans. A **23** (1992) 785-795.

13) C. Zener: Trans. AIME **167** (1946) 550-595.

14) W. Steven and A. G. Haynes: J. Iron Steel Inst. **183** (1956) 349-359.

15) Z. Zhao, C. Liu, Y. Liu and D. O. Northwood: J. Mater. Sci. **36** (2001) 5045-5056.

16) L. C. Chang: Metall. Mater. Trans. A **30** (1999) 909-915.

17) R. L. Bodnar, T. Ohhashi and R. I. Jaffee: Metall. Trans. A **20** (1989) 1445-1460.

18) P. Payson and C. H. Savage: Trans. ASM **33** (1944) 261280.

19) L. A. Carapella: Metal. Progress **46** (1944) 108-118.

20) E. S. Rowlan and S. R. Lyle: Trans. ASM **37** (1946) 27-47

21) R. A. Grange and H. M. Stewart: Trans. AIME **167** (1946) 467-490.

22) A. E. Nehrenberg: Trans. AIME **167** (1946) 494-498.

23) K. W. Andrews: J. Iron Steel Inst. **203** (1965)721-727.

24) G. Ghosh and G. B. Olson: Acta Metall. Mater. **42** (1994) 3361-3370.

25) C. Capdevila, F. G. Caballero and C. García de Andrés: Mater. Sci. Technol. **19** (2003) 581-586.

26) C. Capdevila, F.G. Caballero and C. García de Andrés: ISIJ Int. **42** (2002) 894-902.

27) C. Capdevila, F. G. Caballero and C. García de Andrés: Materials Algorithms Project, www.msm.cam.ac.uk/map/steel/programs/MS.neural.htm.

28) C. García de Andrés, F. G. Caballero, C. Capdevila and L. F. Álvarez: Mater. Charact. **48** (2002) 101-111.

29) G. F. Vander Voort: *Metallography. Principles and Practice,* (McGraw-Hill Book Company, New York, U.S.A., 1984) pp.426-428.

30) D. B. Wiles and R. A. Young: J. Appl. Cryst. **14** (1981) 149-151.

31) C. García de Andrés, M. J. Bartolomé, C. Capdevila, D. San Martín, F. G. Caballero and V. López: Mater. Charact. **46** (2001) 389-398.

32) MTDATA: Phase Diagram Calculation Software, National Physical Laboratory, Teddington, UK, 2004.

33) H. K. D. H. Bhadeshia: Materials Algorithms Project, www.msm.cam.ac.uk/map/steel/programs/mucg46-b.html.

34) H. I. Aaronson, H. A. Domain, and G. M. Pound: Trans. Met. Soc. AIME **236** (1966) 753-767.

35) H. I. Aaronson, H. A. Domain, and G. M. Pound: Trans. Met. Soc. AIME **236** (1966) 768-780.

36) H. K. D. H. Bhadeshia and D. V. Edmonds: Acta Metall. **28** (1980) 1265-1273.

37) A. Ali and H. K. D. H. Bhadeshia: Mater. Sci. Technol. **6** (1990) 781-784.

38) S. S. Babu and H. K. D. H. Bhadeshia: J. Mater. Sci. Lett. **14** (1995) 314-316.

39) S. B. Singh, H. K. D. H. Bhadeshia: Mater. Sci. Eng. A **245** (1998) 72-79.

40) S. B. Singh and H. K. D. H. Bhadeshia: Materials Algorithms Project, www.msm.cam.ac.uk/map/neural/programs/plate-b.html.

41) C. H. Young and H. K. D. H. Bhadeshia: Mater. Sci. Technol. **10** (1994) 209-214.

42) A. Matsuzaki and H. K. D. H. Bhadeshia: Mater. Sci. Technol. **15** (1999) 518-522.

43) D. Quidort and Y. J. M Brechet: ISIJ Int. **42** (2002) 1010-1017.

44) M. Umemoto, K. Horiuchi and I. Tamura, Trans. Iron Steel Inst. Jpn. **22** (1982) 854-861.

45) H. K. D. H. Bhadeshia and D. V. Edmonds: Metall. Trans. A **10** (1979) 895-907.

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Figure 10　5 and 50 % bainite TTT curves for the studied steel.

Tables and Figures

Table 1   Chemical compositions of the studied steel in wt.-%.

C	Mn	Cr	Ni	Si	Mo	V	S
0.31	1.22	0.14	0.10	0.25	0.03	0.004	0.01

Table 2   Calculation of M_s temperature

Empirical formulas or Model	Martensite start temperature, M_s /ºC
Experimental value	*342*
Empirical Formulas:	
Payson and Savage [18]	355
Carapella [19]	348
Rowland and Lyle [20]	351
Grange and Stewart [21]	376
Nehrenberg [22]	361
Steven and Haynes [14]	369
Andrews [23]	363
Thermodynamic Theory:	
Ghosh and Olson [24]	349
Neural Network Analysis:	
Capdevila et al [27]	350

Table 3   Calculation of B_s temperature

Empirical formulas or Model	Bainite start temperature B_s (ºC)
Experimental value	*525*
Empirical Formulas:	
Steven and Haynes [14]	621
Zhao *et al.* [15]	559
Bodnar *et al.* [17]	570
Bainite Theory:	
Bhadeshia [33]	515

Table 4 Overall activation energy $Q_{0.5}^{*}$ for 50% reaction.

Microstructure	Overall activation energy for 50% reaction, $Q_{0.5}^{*}$ / kJ·mol^{-1}
Upper bainite (525 ℃-475 ℃)	17
Lower bainite (425 ℃-375 ℃)	16

(a)

50 μm

(b)

50 μm

(c)

CENIM   SEI   7.0kV   1μm   WD 4.3mm