Austenite Grain Size and the Martensite–Start Temperature

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Abstract

New experimental evidence is obtained to confirm the dependence of the martensite–start temperature on the austenite grain size. The Fisher model for the geometrical partitioning of austenite grains by plates of martensite is used here to develop a theory to explain the observations, based on the ability to detect transformation as a function of the austenite grain size. The relationship derived has been tested on a range of published data.

There have been several studies on the dependence of the martensite–start temperature (M_S) on the austenite grain size [1–4]. The austenitisation temperature also affects M_S [5, 6] but only via the associated variation in austenite grain size [7]. In another context, the stability of retained austenite to martensitic transformation increases as the former is refined in a mixed microstructure [8–12].

There have been many qualitative explanations of such observations. One argument is that a refinement of the austenite grain size (L_γ) leads to the Hall–Petch strengthening of austenite, thereby making it difficult for martensite to form [1]. It is known that solid–solution strengthening affects the nucleation of martensite and bainite, by providing a greater resistance to the motion of dislocations involved in the nucleation process [13]. On the other hand, the Hall–Petch theory relies on the transmission of slip *across* grain boundaries, whereas any resistance to the motion of dislocations at the nucleation stage has to be more localised. Indeed, the equations for the activation volume in the thermally activated motion of the martensite/austenite interface relate only to the volume of material swept by the interface between the parent and nucleus [14, 15].

An alternative explanation in the case of highly alloyed steels is based on a burst phenomenon in which a large fraction of the austenite transforms into martensite within a very small temperature interval [16–18]. The tendency for a burst to occur decreases as the austenite grain size is refined [19]. This is explained qualitatively by the fact that the stress concentration at a martensite plate–tip scales with the size of the plate, which in turn is related to the austenite grain size. Transformation is therefore detected at a higher temperature for large grains [7, 16].

However, most martensitic steels do not undergo bursts of transformation and especially those which have a low alloy content and form lath–like martensite. There is a gradual increase in the fraction of martensite as a function of undercooling below the M_S temperature, roughly following the classical Koistinen and Marburger equation [20]. In such circumstances, the common qualitative explanation for the austenite grain size effect comes from a geometrical partitioning model by Fisher *et al.* [21]. The volume fraction of martensite formed in the early stages of transformation is proportional to the cube of the austenite grain size. Thus the fraction of transformation needed to detect M_S is reached at a smaller undercooling when the austenite grain size is large.

It is the purpose of this paper to develop this model of geometrical partitioning, into a quantitative framework which allows the estimation of M_S variation as a function of the austenite grain size. None of the relevant publications in which dilatometric measurements have been used to measure M_S have reported the exact method of noting the expansion due to martensite formation in order to fix the start–temperature. New experiments have therefore been conducted to verify the grain size effect for low–alloy steels, using a dilatometric method which is objective in the determination of the early stages of transformation [22].

Experimental Work

Details of the experimental method for measuring the transformation temperature using a push–rod *BAHR DIL805* high–speed dilatometer have been described elsewhere [22]. Each sample was austenitised at 770–1100°C for 30 s, but one of the samples was austenitised at 1100°C for 600 s to obtain the largest austenite grains. The heating rate used was 30°C s^{-1}, giving Ac_1 and Ac_3 temperatures of 660 and 754 °C respectively. The heating and austenitisation treatments were carried out under a vacuum of 5×10^{-4} mbar. Every sample was quenched twice before measure M_S to avoid any effect of initial microstructure. The reported measurements of M_S are from the second quench.

The alloy used was prepared as a solid cylindrical–sample of dimensions 3.6×8 cm by centrifugal casting and then homogenised in a vacuum furnace for two days at 1200 °C. The length of the sample was then cut into six pieces of equal thickness; their individual chemical analyses are shown in Table b. Composition variations of the kind depicted can only influence M_S by ±1°C [22–24]. An advantage of using this particular alloy system is that the cooling rates needed to achieve martensite are already known [22, 25].

Secondly, an offset method [22] is used to ensure that M_S is determined objectively, *i.e.,* independent investigators should reach the same conclusions given identical data. This is because the point at which transformation is said to begin is determined by a positive deviation by a fixed strain (corresponding to 1 volume % of martensite forming at room temperature using the calculated

lattice parameters of the austenite and martensite) [22].

Table 1
Chemical compositions in wt%

Sample	C	Ni	Mn
1	0.124	5.02	2.26
2	0.126	5.03	2.28
3	0.126	5.01	2.26
4	0.126	5.05	2.28
5	0.123	4.97	2.24
6	0.127	5.04	2.28
Average	0.125	5.02	2.27

Saturated aqueous picric acid with wetting agent, 100 ml of saturated picric acid with 4 g of sodium dodecylbenzen sulphate in 100 ml H_2O, were used to reveal the prior austenite structure. The grain size was measured using the mean linear intercept method [26]. The results are presented in Fig. 1a; consistent with previous work [1–4], there is a large dependence of M_S as a function of the austenite grain size. Fig. 1b serves to confirm that the transformation to martensite occurs gradually with undercooling below M_S; the data presented are for the largest austenite grain size which are known to be prone to bursts of transformation in highly alloyed steels [16–19].
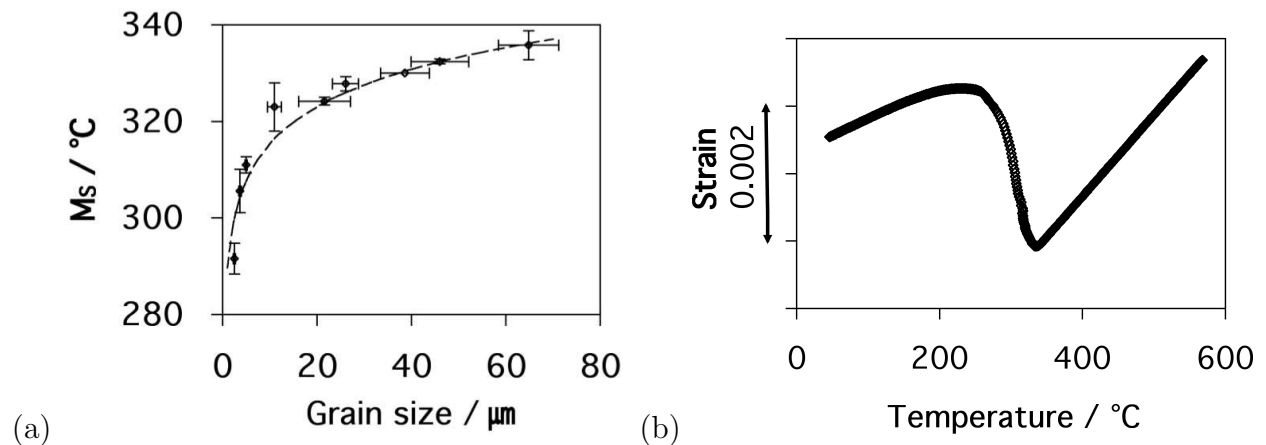

Fig. 1. (a) Measured variation in the martensite–start temperature determined from dilatometric data using the offset method. The uncertainties in M_S are determined as in [22] and those in the grain size as in [26]. The dashed line represents a calculated curve obtained by fitting the experimental data to equation 5 as discussed later. (b) Dilatometer curve for sample austenitised at $1100°C$ for $600\,s$ and cooled at $10°C\,s^{-1}$.

Theoretical Analysis

The model described here begins with the Fisher *et al.* geometric partitioning analysis [21] in which the number of martensite plates per unit volume, N_V is related to the fraction f of martensite as follows:

$$\frac{df}{dN_V} = m(1-f)\overline{V}_C \equiv \frac{m(1-f)}{N_V^C} \tag{1}$$

where m is the aspect ratio of the martensite plate (assumed here to be 0.05 [27]) and $\overline{V}_C$ is the average size of the compartment resulting from the partitioning of an austenite grain by the presence of martensite plates. N_V^C is the number of austenite compartments per unit volume. Each new martensite plate produces one additional compartment so that

$$N_V^C = \frac{1}{V_\gamma} + N_V \tag{2}$$

where V_γ is the average austenite grain volume. On combining equations 1 and 2 we get

$$N_V = \frac{1}{V_\gamma}\left[\exp\left\{-\frac{\ln(1-f)}{m}\right\} - 1\right] \tag{3}$$

This equation can be used to convert the measured martensite fraction into N_V as illustrated in Fig. 2. The trends illustrated in Fig. 2 seem independent of the austenite grain size and can be represented reasonably by an equation of the form

$$N_V = a[\exp\{b(M_S^o - T)\} - 1] \tag{4}$$

where a and b are empirical fitting constants. The term M_S^o is defined as a fundamental martensite–start temperature for an infinitely large austenite grain size; it will be shown later that it can be derived using thermodynamics. On combining equations 3 and 4 we obtain:

$$M_S^o - T = \frac{1}{b}\ln\left[\frac{1}{aV_\gamma}\left\{\exp\left(-\frac{\ln(1-f)}{m}\right) - 1\right\} + 1\right] \tag{5}$$

In this equation, the term $M_S^o - T$ becomes $M_S^o - M_S$ when the fraction f is set to be the first detectable fraction (f_{M_S}) of martensite, and $M_S \rightarrow M_S^o$ as $V_\gamma \rightarrow \infty$.
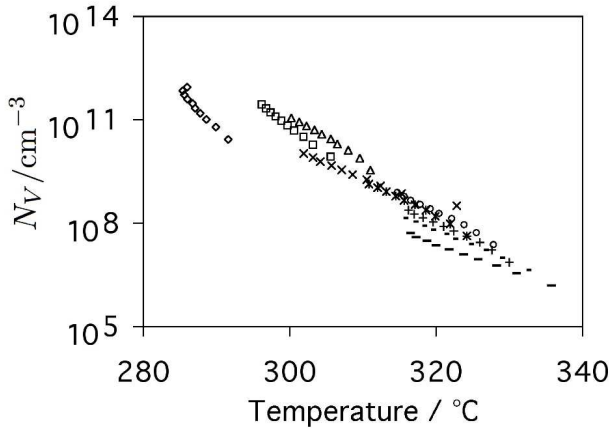

Fig. 2. Calculated number of plates per unit volume as a function of the temperature, for alloy listed in Table 1.

The dashed curve in Fig. 1 shows how equation 5 is able to reproduce the M_S temperature as a function of the austenite grain size with $f_{M_S} = 0.01$ (the offset used in determining the martensite–start temperature [22]); the plate aspect ratio $m = 0.05$ [27]; there are three fitting constants used, $a = 1 \, \text{mm}^{-3}$, $b = 0.2689$ and $M_S^o = 363.5 \, ^\circ\text{C}$.

Given that M_S^o is the highest temperature at which martensite can form, it should be possible to calculate it using thermodynamics alone, but accounting for the stored energy of martensite which is about $700 \, \text{J mol}^{-1}$ [27]. M_S^o is therefore given by the temperature at which $G_\gamma - G_\alpha = 700 \, \text{J mol}^{-1}$, where G_α and G_γ are the Gibbs free energies of ferrite and austenite of the same chemical composition; the free energies were calculated using MTDATA and the TCFE database [28]. The assumption in calculating M_S^o in this way is that the highest martensite–start temperature should be determined by a thermodynamic energy balance alone, with no consideration given to kinetic effects.

In order for the model to be useful over a broad range of steels it is necessary to obtain generally applicable values of the fitting constants a and b, even if it means some sacrifice of accuracy. This was done by fitting equation 5 to the combined data from the low–alloy steels listed in Table 2, which transform gradually with increasing undercooling below the M_S temperature. The resulting curve, Fig. 3, was then used to make predictions on a wider range of steels which contain large concentrations of solutes; Fe–27Ni–0.025C wt% [1], Fe–32Ni wt% [29] and Fe–30Pd at% [30]. The method is seen to reasonably represent all of these experiments.

In summary, equation 5 and the values of a and b obtained in Fig. 3 can be used to make quantitative estimates of the dependence of the observed M_S on the austenite grain size.
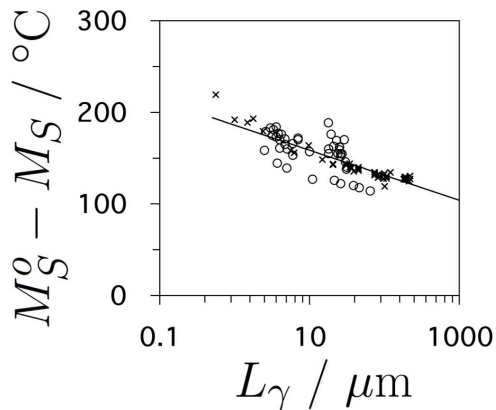

Fig. 3. Suppression of M_S^o as a function of the austenite grain size. Circles represent low–alloy steel data from the present work and [2, 31], which were used to derive the plotted line ($a = 1.57 \times 10^{-21} \, \mu\text{m}^3$ and $b = 0.253$). Crosses are data from rich alloys of iron [1, 29, 30].

Table 2
Thermodynamically calculated values of the temperature M_S^o.

Alloy / wt%	$M_S/^\circ\text{C}$	$M_S^o/^\circ\text{C}$	Reference
Fe–0.13C–5Ni–2.27Mn	292–336	450	present work
Fe–0.39C–0.65Mn–0.24Si–1.6Ni–0.67Cr–0.15Mo	281–330	470	[2]
Fe–0.15C–1.9Mn–0.2Si–0.2Cr–0.03Al	361–393	545	[31]

References

[1] P. J. Brofman, G. S. Ansell: Metallurgical Transactions A 14A (1983) 1929–1931.

[2] S. J. Lee, Y. K. Lee: Materials Science Forum 475–479 (2005) 3169–3172.

[3] J. Huang, Z. Xu: Materials Science & Engineering A A438–440 (2006) 254–257.

[4] G. S. Ansell, P. J. Brofman, T. J. Nichol, G. Judd: Effect of austenite strength on the transformation to martensite in Fe–Ni and Fe–Ni–C alloys: in: G. B. Olson, M. Cohen (Eds.), International Conference on Martensitic Transformations ICOMAT '79: 1979: pp. 350–355.

[5] O. A. Ankara, A. S. Sastri, D. R. F. West: JISI 204 (1966) 509–511.

[6] T. Maki, S. Shimooka, I. Tamura: Metallurgical Transactions 2 (1971) 2944–2955.

[7] M. Umemoto, W. S. Owen: Metallurgical Transactions 5 (1974) 2041–2046.

[8] W. C. Leslie, R. L. Miller: ASM Transactions Quarterly 57 (1964) 972–979.

[9] H. K. D. H. Bhadeshia, D. V. Edmonds: Metal Science 17 (1983) 411–419.

[10] H. K. D. H. Bhadeshia, D. V. Edmonds: Metal Science 17 (1983) 420–425.

[11] B. V. N. Rao, M. S. Rashid: Metallography 16 (1983) 19–37.

[12] F. G. Caballero, C. G. Mateo, J. Chao, M. J. Santofimia, C. Capdevila, C. G. de Andrés: ISIJ International 48 (2008) 1256–1262.

[13] G. Ghosh, G. B. Olson: Acta Metallurgica and Materialia 42 (1994) 3361–3370.

[14] G. B. Olson, H. K. D. H. Bhadeshia, M. Cohen: Acta Metallurgica 37 (1989) 381–389.

[15] G. B. Olson, H. K. D. H. Bhadeshia, M. Cohen: Metallurgical & Materials Transactions A 21A (1990) 805–809.

[16] J. C. Bokros, E. R. Parker: Acta Metallurgica 11 (1963) 1291–1301.

[17] R. Brook, A. R. Entwisle: Journal of the Iron and Steel Institute 203 (1965) 905–912.

[18] D. S. Sarma, J. A. Whiteman, S. R. Keown: Journal of Materials Science 14 (1979) 693–698.

[19] J. R. C. Guimarães, J. C. Gomes: Acta Metallurgica 26 (1978) 1591–1596.

[20] P. K. D, R. E. Marburger: Acta Metallurgica 7 (1959) 59–60.

[21] J. C. Fisher, J. H. Hollomon, D. Turnbull: Metals Transactions 185 (1949) 691–700.

[22] H.-S. Yang, H. K. D. H. Bhadeshia: Materials Science and Technology 23 (2007) 556–560.

[23] H. K. D. H. Bhadeshia: Metal Science 15 (1981) 178–150.

[24] H. K. D. H. Bhadeshia: Metal Science 15 (1981) 175–177.

[25] H.-S. Yang, H. K. D. H. Bhadeshia: Materials Science and Technology 24 (2008) 335–342.

[26] R. T. DeHoff, F. N. Rhines: Quantitative Microscopy: McGraw Hill, New York, 1968.

[27] J. W. Christian: Thermodynamics and kinetics of martensite: in: G. B. Olson, M. Cohen (Eds.), International Conference on Martensitic Transformations ICOMAT '79: 1979: pp. 220–234.

[28] NPL: MTDATA: Software, National Physical Laboratory, Teddington, U.K. (2006).

[29] R. Huang, L. Xi, X. Li, C. R. Liu, H. Qiu, J. Lee: Mechanical Systems and Signal Processing 21 (2006) 193–207.

[30] K. Seki, H. Kura, T. Sato, T. Taniyama: Journal of Applied Physics 103 (2008) 063910.

[31] A. García-Junceda, C. Capdevila, F. G. Caballero, C. G. de Andrés: Scripta Materialia 58 (2008) 134–137.