Uncertainties in dilatometric determination of martensite start temperature

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Methods for the dilatometric determination of the martensite start temperature of steels are discussed, with emphasis on noise in the experimental data. The methods are tested on a new set of experiments using a specially prepared steel. Relying on the first detection of expansion due to transformation is fraught with difficulties. Instead, an offset method is proposed which should enable independent investigators to reach the same conclusions given identical data. The technique at the same time preserves the notion that the early stages of martensite formation correspond to the start temperature. The uncertainty in the start temperature deduced using this method is about ±12°C, better than the reported values of noise in published data. The work underlines the need to state the sensitivity of the analysis technique when quoting transformation temperatures.

Keywords: Dilatometry, Martensite, Transformations, Steels

Introduction

There is a change in density when martensite forms in steels, which can be measured using dilatometry. Most dilatometers are of the push rod type and hence are limited to detecting the length change due to the volume strain accompanying solid state reactions. One of the parameters that can be extracted from the plot of the change in length as a function of the temperature is the martensite start M_S temperature. A deviation of the length from that expected due to thermal contraction is taken to imply transformation. This raises difficulties in that the extent of deviation must be defined and the procedure used in not always clear. In some recent work, the M_S has been identified beyond the point where the curve departs significantly from thermal contraction at a higher temperature.[1]

Even for the case where the definition of M_S is the point where expansion is detected, uncertainties exist because the output of a dilatometer is never perfect; the data contain noise which is mostly ignored when measurements are reported. The purpose of the present work was to examine systematically the effect of this noise on the determination of the M_S temperature. The work was inspired when attempts were made to verify certain theoretical predictions of transformation temperatures; the choice of the alloy is consistent with the aims of that wider study.[2,3] The present experiments are concerned with martensite in a high hardenability steel, but the methodology presented should be generally applicable in the interpretation of dilatometric data.

The primary aim is to define a method which enables independent assessments of the same dilatometric data to reach identical numerical conclusions.

Experimental

A technique usually applied to manufacture standards for chemical analysis was used to make the alloys. A solid cylindrical sample of dimensions 3·6 × 8 cm was centrifugally cast and then homogenised in a vacuum furnace for 2 days at 1200°C. The length of the sample was then cut into five pieces of equal thickness; their individual chemical analyses are shown in Table 1. The carbon concentration was analysed using a LECO analyser to a reproducibility of ±0·0013 wt-%, and the remaining elements using spark optical emission spectroscopy to a reproducibility of ±0·003 wt-%. These chemical composition data can be used to estimate the expected variation in the martensite start temperature. Using the methodology described elsewhere,[4,5] the variation expected on the basis of the tabulated compositions is estimated to be just ±1°C.

Cylindrical dilatometric samples of diameter 4 mm and length 7 mm were machined, some of which were made hollow by drilling a 3 mm diameter longitudinal hole.

A push rod BAHR DIL805 high speed dilatometer with radio frequency induction heating was used. The sample temperature is measured by a thermocouple welded to its surface using a precision welder and jig supplied by the dilatometer manufacturer. Each sample was austenitised at 950°C for 3 min, followed by cooling at a constant rate to ambient temperature. The cooling rates used were in the range 3·2–330°C s^{-1}. It was not possible to maintain a constant cooling rate when $\dot{T} \geqslant 140$°C s^{-1}, so the stated values in those cases are over the range 300–500°C.

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Table 1 Chemical composition of samples, wt-%

Sample	Mn	Ni	C
1	2·28	4·04	0·132
2	2·28	4·04	0·132
3	2·28	4·03	0·130
4	2·25	4·02	0·132
5	2·28	4·03	0·130
Average	2·274	4·032	0·1312

The heating rate used was 30°C s^{-1}, giving A_{C1} and A_{C3} temperatures of 652 and 751°C. The heating and austenitisation treatments were carried out under a vacuum of 5×10^{-4} mbar, and the cooling was achieved using helium or argon gas.

For the sample size used, the resolution of the BHAR dilatometer is 50 nm, corresponding to a strain of $7{\cdot}1\times10^{-6}$ and a martensite volume fraction of $1{\cdot}1\times10^{-3}$ at 400°C.

The full set of experimental measurements are recorded in Table 2 for subsequent discussion.

Detection of expansion

The thermal expansion coefficient of austenite, determined over the temperature range 420–650°C was found in 16 separate experiments to be constant, with correlation coefficients in the range 0·99994–0·99999 in the plot of thermal strain versus temperature. It is reasonable therefore to assume that the austenite contracts linearly as the temperature is reduced. The thermal expansion coefficient of austenite from these experiments was found to be $2{\cdot}43\times10^{-5}\pm0{\cdot}13\times10^{-5}{}^{\circ}\mathrm{C}^{-1}$, where the error is a single standard deviation.

It is common to take the first onset of expansion during cooling to correspond to the start temperature, but it is necessary to take account of noise. The root mean square level of noise in fitting a straight line to the thermal contraction of austenite was determined experimentally to be equivalent to a strain ε of $\pm1{\cdot}65\times10^{-5}$ which is greater than the resolution of the equipment ($7{\cdot}1\times10^{-6}$).

The expansion method relies on the detection of a deviation from the linear thermal contraction curve of austenite. This latter curve can be fixed by fitting a linear regression line to the data, yielding a slope m and an intercept C

$$\varepsilon_\gamma = mT + C \qquad (1)$$

where ε_γ is the measured strain as the austenite cools and T is the temperature. However, the slope and intercept are associated with standard errors, so four lines can be plotted ($m\pm\Delta m$, $C\pm\Delta C$), defining the upper and lower 95% confidence limits to the austenite contraction curve.

Figure 1 illustrates how, using the lines ($m+\Delta m$, $C+\Delta C$) and ($m-\Delta m$, $C-\Delta C$), the upper and lower bound M_S values given in Table 2 were obtained. The uncertainty particularly in the upper estimate of M_S is large because the curvature of the dilatometer output in that region is small. For this reason it was not possible in some cases, using this method, to define the martensite start temperatures. Two examples emphasising that this method is unlikely to give reliable and reproducible results are illustrated in Fig. 2.

The situation did not improve at all when the lines ($m+\Delta m$, $C-\Delta C$) and ($m-\Delta m$, $C+\Delta C$) were used. A larger number of cases occurred in which clear solutions did not exist. Finally, it is worth noting that taking the derivative of the strain versus temperature curve does not help improve the assessment of the dilatometric data. The derivative itself suffers from noise in the slope as is evident by differentiating equation (1), where the error Δm in the slope is retained. Furthermore, additional problems arise because the derivative has to be calculated from discrete, noisy data. This is illustrated in Fig. 3, where the horizontal line represents the expansion coefficient of austenite. Since the expansivity of ferrite in all but the invar steels is always smaller,[6] M_S is defined by the point where the expansivity falls below that of the austenite.

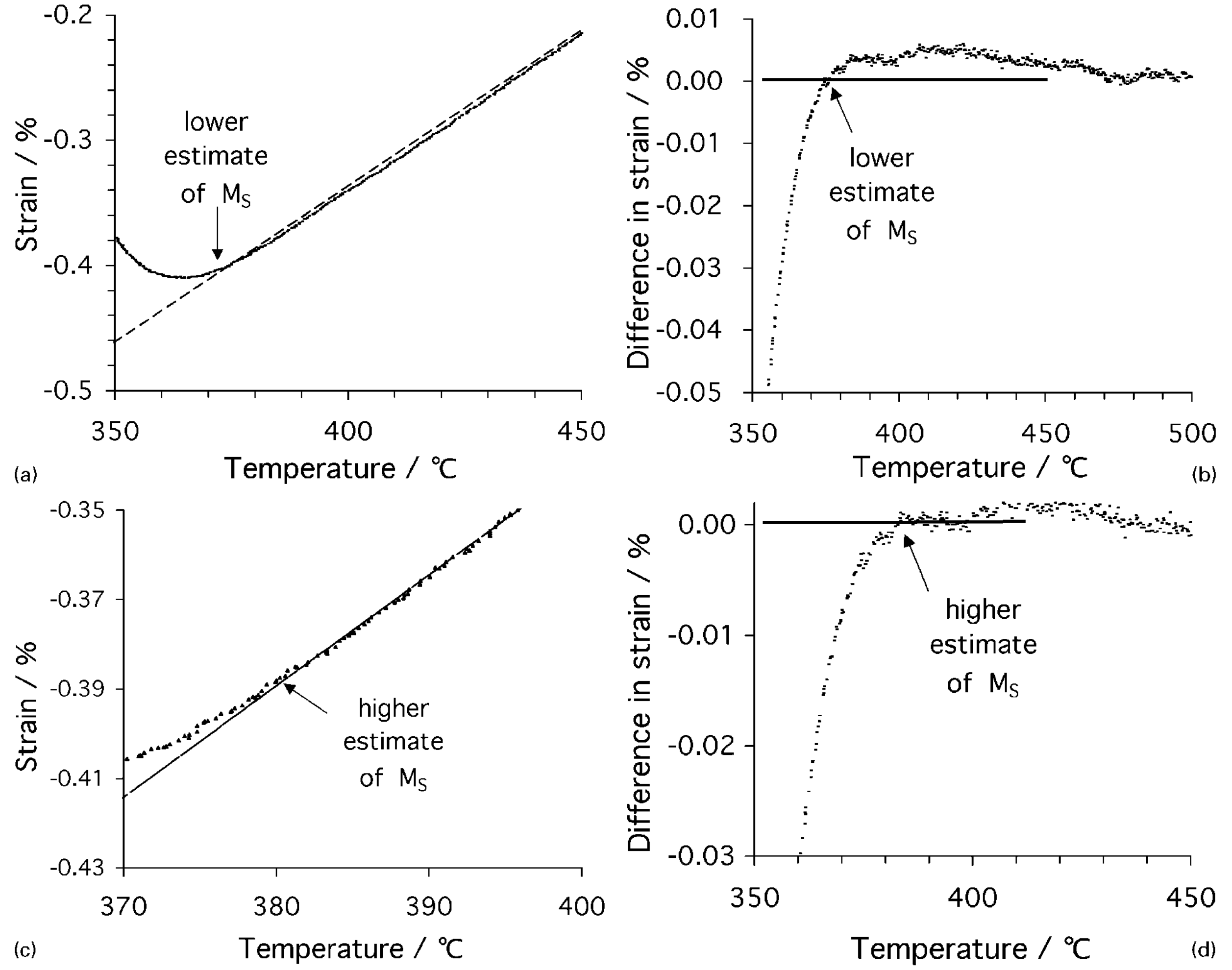
Offset method

The offset method is routinely used in defining the proof strength of materials when the stress–strain curve is

Table 2 Martensite start temperatures as function of technique, for solid and hollow samples*

		Expansion method M_S, °C			Offset method M_S, °C
Sample	$\dot{T}$, °C s^{-1}	Lower	Upper	Mean	$\varepsilon=1{\cdot}21\times10^{-4}$
4, solid	3·2	439	470	455	377
4, solid	5·3	440	504	472	376
4, solid	7·9	420	448	434	363
5, solid	15·8	441	512	477	372
4, solid	15·8	385	412	399	358
5, solid	63·3	435	529	482	363
3, solid	140	379	395	387	361
3, hollow	31·7	444	504	474	401
3, hollow	47·5	441	494	468	392
1, hollow	95	375	383	379	366
3, hollow	95	378	390	384	372
3, hollow	95	423	524	474	370
3, hollow	330	403	409	426	385
2, hollow	330	393	–	–	375
3, hollow	330	–	–	–	374
3, hollow	330	367	372	370	365
Mean		411	456	434	373
σ		29	57	43	12

*The sample numbers in the first column correspond to those in Table 1; σ is the standard deviation and $\dot{T}$ the cooling rate.



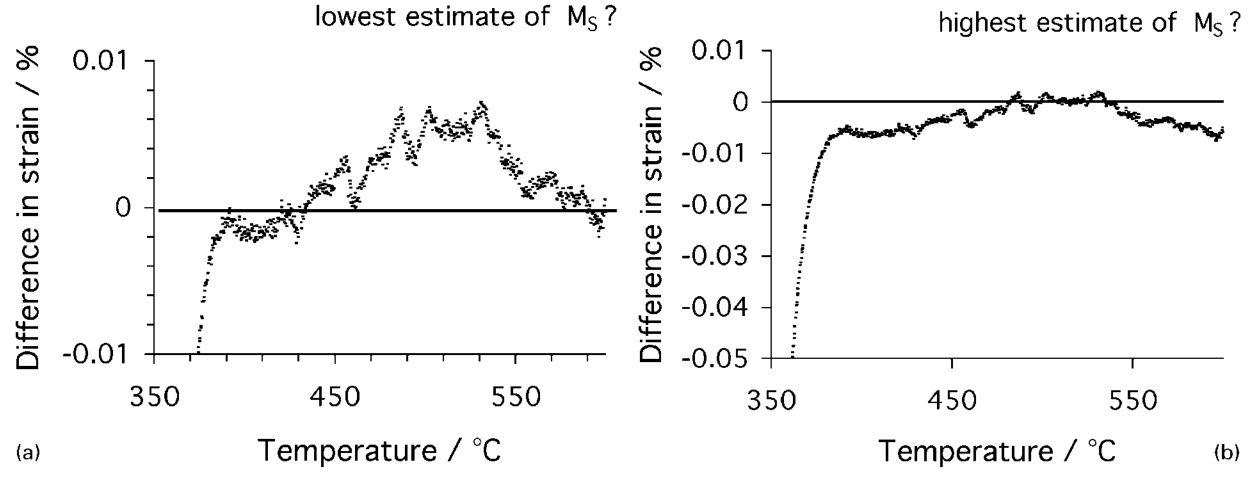
a lower bound of M_S temperature using ($m+\Delta m$ and $C+\Delta C$); *b* as *a*, but difference between fitted line and experimental data plotted on ordinate; *c* upper bound of M_S temperature using ($m--\Delta m$ and $C-\Delta C$); *d* as *c*, but difference between fitted line and experimental data plotted on ordinate

1 Analysis of dilatometric data for hollow sample 1 cooled at 95°C s^{-1}: Table 2

smooth, making it difficult to define the deviation from elastic deformation. In the case of a tensile test, it is conventional to offset the test line by a strain of 0·2% in order to define the proof strength. A similar procedure could be followed for martensite as illustrated in Fig. 4.

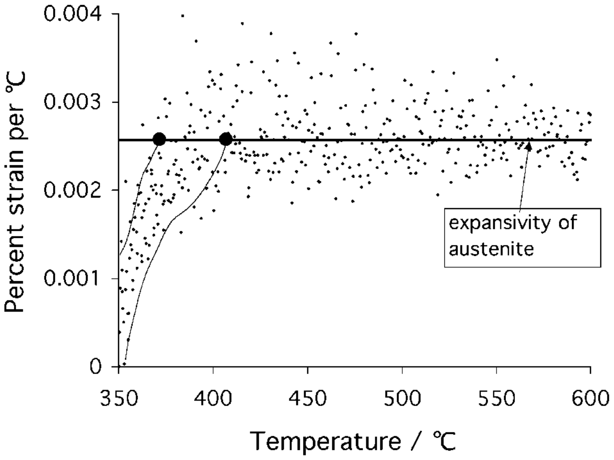
The question then arises as to the magnitude of the transformation strain that should be used as the offset from the thermal contraction curve of austenite in order to determine the martensite start temperature.

A transformation strain due to 1 vol.-% martensite can be set as the value of the offset at which M_S is measured. For the present steel, it will be shown that this corresponds to a strain of $1{\cdot}21\times10^{-3}$, which is some two orders of magnitude greater than the noise in the



a lower bound of M_S temperature using ($m+\Delta m$ and $C+\Delta C$); *b* upperbound of M_S temperature using ($m-\Delta m$ and $C-\Delta C$)

2 Lack of clarity in determination of M_S: analysis of dilatometric data for hollow sample 3 cooled at 330°C s^{-1}: Table 2



3 Derivative of strain versus temperature dilatometric curve, plotted versus temperature: each derivative is calculated from three successive strain data; two large points identify $\pm 1\sigma$ uncertainty in M_S and curves are polynomial fits to low temperature data, displaced by $\pm 1\sigma$ about best fit

instrument and should be sufficient for the offset line to intersect the experimental curve in a region of sufficient curvature, thus ensuring a reliable measure of M_S.

The transformation strain depends of course on the alloy studied. The strain cannot be measured directly from the dilatometer curve since the martensite reaction may not reach completion at the point where the experiment is terminated. The critical strain corresponding to 1 vol.-% martensite can be calculated if the lattice parameters a_γ and a_α of austenite and martensite respectively are known. The following equations are available from compiled data[7]

$$\begin{aligned} a_\alpha = {} & 0{\cdot}28664 + \\ & [(a_{Fe} - 0{\cdot}0279x_C^\alpha)^2(a_{Fe} + 0{\cdot}2496x_C^\alpha) - a_{Fe}^3]/(3a_{Fe}^2) \\ & - 0{\cdot}003x_{Si}^\alpha + 0{\cdot}006x_{Mn}^\alpha + 0{\cdot}007x_{Ni}^\alpha + 0{\cdot}031x_{Mo}^\alpha + \\ & 0{\cdot}005x_{Cr}^\alpha + 0{\cdot}0096x_V^\alpha \end{aligned} \tag{2}$$

where x_i^α represents the mole fraction of species i in phase α. The lattice parameter of pure iron a_{Fe}= 0·28664 nm (Ref. 8). The equation applies at room temperature (25°C).

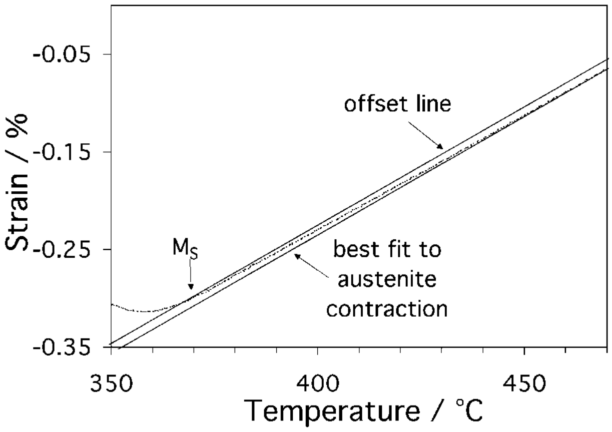
The parameter for austenite at room temperature is given by[9]

$$a_\gamma = 0{\cdot}3573 + \sum_{i=1}^{n} c_i w_i^\gamma \tag{3}$$

where w_i represents weight fraction and

$$\begin{aligned} \sum_{i=1}^{n} c_i w_i^\gamma = {} & 3{\cdot}3 \times 10^{-1} w_C^\gamma + 9{\cdot}5 \times 10^{-3} w_{Mn}^\gamma \\ & - 2 \times 10^{-3} w_{Ni}^\gamma + 6 \times 10^{-3} w_{Cr}^\gamma \\ & 3{\cdot}1 \times 10^{-2} w_{Mo}^\gamma + 1{\cdot}8 \times 10^{-2} w_V^\gamma \end{aligned}$$

Given that the austenite unit cell contains 4 iron atoms and that of martensite 2 per cell, the offset strain ε_O corresponding to a specified value of martensite fraction V is given by



4 Offset method illustrated

$$(1 + \varepsilon_O)^3 = a_\gamma^{-3}[2Va_\alpha^3 + (1 - V)a_\gamma^3] \tag{4}$$

The essence of the offset method is unlikely to be a new concept in the context of dilatometry. However, it is important to note that the method for calculating the critical value ε_O of the offset strain leads to an entirely reproducible value of M_S. The last column of Table 2 shows the results calculated in this way.

It is worth noting that the average value of the M_S temperature, measured using the offset method, changes from 419, 384, 382 to 373 as the volume percentage of martensite at which M_S is measured is changed from 0·08, 0·5, 0·54 and 1% respectively. Although this appears at first sight to be awkward, it is well established that the M_S temperature depends on the sensitivity of the technique used. Thus, acoustic emission can be much more sensitive than electrical resistivity measurements, so the M_S temperature measured using the latter technique is much lower than associated with acoustic data.[10]

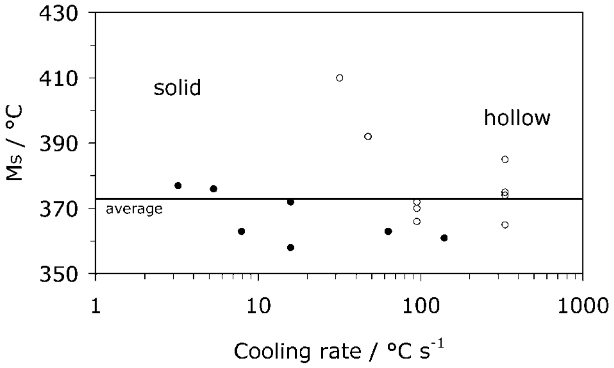
Consequently, in situations where it is important, it would be good practice to quote both the M_S temperature and the offset ε_O used in its definition.

The offset method clearly is more reliable than the expansion method. This is also evident in Table 2 where the standard deviation of the measurements is smaller for the offset method with $\sigma = \pm 12°C$. It is useful to compare this with the noise perceived when large quantities of M_S data are analysed using a neural network method based on a Bayesian framework.[11,12] One advantage of a Bayesian framework is that it avoids overfitting to the data and hence should give a reliable estimate of noise in the reported M_S values.[13,14] The perceived normalised noise in the M_S is $\sigma \simeq \pm 0{\cdot}04$. Taking the M_S temperature as 373°C, $\sigma = \pm 15°C$ is obtained. That this is larger than reported here for the offset method might be expected since the neural networks rely on large quantities of data compiled from diverse sources. In other neural network analyses not using a Bayesian framework, the standard error in the M_S was found to be ±15·3°C[15] and ±12°C.[16]

In contrast, the standard deviation in the M_S data determined using the expansion method is unrealistically large at $\sigma = \pm 43°C$.

Sources of error

The equipment used in the present work has a much higher spatial resolution than the noise detected in the



5 M_S temperatures using offset method, for solid and hollow specimens as function of cooling rate

experimental data. A standard deviation of 12°C in the M_S measurements using the offset method is large and as pointed out earlier, cannot be accounted for by variations in the chemical composition.

A contribution to the observed variations in M_S may arise from the fact that the samples do not achieve a uniform temperature during the experiments. Figure 5 shows a comparison between the data for the solid and hollow samples. There is no systematic difference between the two kinds of specimens indicating that even the hollow samples may not achieve a sufficiently uniform temperature during cooling. An additional explanation is that the early stages of martensitic transformation are sensitive to the initial austenite grain structure,[17–19] in which case there is no guarantee that identical grain structures are generated in every sample. Martensitic nucleation can occur from arrays of dislocations associated with grain boundaries and therefore may be sensitive to the nature of those boundaries.[20]

Conclusions

A method is proposed in which dilatometric data are interpreted by defining the first onset of transformation to be that at which a critical strain is achieved relative to the thermal contraction of the parent phase. The critical strain is calculated for 1 vol.-% martensitic transformation assuming that the latter occurs at room temperature, by using equations for the lattice parameters of austenite and martensite. This ensures that the method is reproducible and emphasises that transformation start temperatures should be quoted with the value of the critical strain used to interpret the dilatometric data.

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