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Application of non-isothermal dilatometry for evaluation of kinetic parameters in non-reversing reactions

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The applicability of the non-isothermal dilatometric technique for the investigation of rate processes is discussed. Equations have been derived for a non-reversing reaction, which may be used to calculate the kinetic parameters from non-isothermal dilatometric curves. The main advantages of the approach are considerable economies in experimental procedure and the avoidance of experimental errors associated with the onset of reaction before isothermal conditions are attained. The position of the inflection point on the dilatometric curve and the slope at that point give the activation energy and frequency factor of the reaction. The usefulness of the new approach is demonstrated by the good agreement between values of activation energy obtained by the new equations and reported literature values for the second and third stages in the tempering reaction of a plain carbon steel.

1. Introduction

In general, phenomenological kinetic reaction parameters such as activation energy and frequency factor have been utilized as the means of appreciating the thermal stability of a reaction. So far, the kinetic reaction parameters have been evaluated by isothermal measurements, taken as a function of time t and temperature T, of physical properties, e.g. specific volume/length, electrical resistivity and magnetization. However, experiments are frequently performed in a non-isothermal fashion, e.g. the tempering of steel and hydrogen escape from trapping sites in the steel. An isothermal study has the disadvantage that it requires considerable time and experimental data. In addition, when a sample undergoes considerable reaction in being raised to the temperature of interest, the results obtained by the method are questionable.

There has therefore been an increasing demand for developing an isochronal method in which considerably less time and experimental data are required than in the isothermal method, while the kinetics can be probed over an entire temperature range in a continuous manner without any data gaps. It is the purpose of this paper to derive equations for analysing phenomenological kinetic parameters, i.e. activation energy and frequency factor, in non-reversing reactions from non-isothermal dilatometric curves. The approach is applied to the second and third stages of the tempering of hardened plain carbon steels, which has been selected to serve as an example since dilatometric analysis has been made previously, thus allowing comparison [1–3].

2. Derivations

Assume that we start with $\Delta L_0/L$ of the initial specimen length and that the specimen length at time t is $\Delta L_t/L$ and the final specimen length $\Delta L_f/L$. We then assume that the length fraction of reactant left (active mass) is defined as

$$C = \left(\frac{\Delta L_t}{L} - \frac{\Delta L_f}{L}\right)\Big/\left(\frac{\Delta L_0}{L} - \frac{\Delta L_f}{L}\right) \tag{1}$$

Provided that the tempering reaction under consideration is of the order n, the rate expression is then given by

$$\frac{-\mathrm{d}C}{\mathrm{d}t} = kC^n \tag{2}$$

where k is the specific rate. It is assumed that the specific rate may be expressed relative to temperature by

$$k = Z\exp\left(\frac{-E}{RT}\right) \tag{3}$$

where Z is the frequency factor, E is the activation energy, R is the gas constant and T is the temperature. Solving for k in Equation 2 and substituting into Equation 3 for k gives

$$\frac{-\mathrm{d}C}{\mathrm{d}t} = ZC^n\exp\left(\frac{-E}{RT}\right) \tag{4}$$

If Φ is defined as a fixed heating rate, $\mathrm{d}T/\mathrm{d}t = \Phi$, then

$$\frac{\mathrm{d}C}{\mathrm{d}T} = \left(\frac{\mathrm{d}C}{\mathrm{d}t}\right)\left(\frac{\mathrm{d}t}{\mathrm{d}T}\right) = -\frac{ZC^n}{\Phi}\exp\left(\frac{-E}{RT}\right) \tag{5}$$

Differentiation of Equation 5 gives

$$\frac{\mathrm{d}^2C}{\mathrm{d}T^2} = -\frac{Z}{\Phi}\exp\left(\frac{-E}{RT}\right)\left[nC^{n-1}\left(\frac{\mathrm{d}C}{\mathrm{d}T}\right) + C^n\left(\frac{E}{RT^2}\right)\right] \tag{6}$$

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TABLE I Chemical composition of steel (wt %)

C	Mn	Si	P	S
0.94	0.44	0.028	0.009	0.008

The second derivative, Equation 6, disappears at the inflection point of the curve plotted as the length fraction of reactant left against temperature. Setting the right-hand side of Equation 6 equal to zero gives

$$E = -nRT_i^2 C_i^{n-1} \left(\frac{dC}{dT}\right)_i \bigg/ C_i^n \tag{7}$$

where T_i, C_i and $(dC/dT)_i$ are the temperature, length fraction of reactant left and slope of a tangent at the inflection point of the curve plotted as the length fraction of reactant left against temperature, respectively. Z is then calculated from

$$Z = -\frac{\Phi}{C_i^n}\left(\frac{dC}{dT}\right)_i \exp\left(\frac{E}{RT_i}\right) \tag{8}$$

3. Experimental procedure, results and discussion

The applicability of the method was demonstrated by the evaluation of the kinetic parameters of the second and third stages in the tempering reaction of 0.94% plain carbon steels (Specimens A, B and C). The chemical composition is shown in Table I. Heat treatment and volume fraction of retained austenite of the steel are given in Table II. Quantitative analysis of the volume fraction of retained austenite was made by X-ray diffraction measurements using a step scan (operated at $0.025° \sec^{-1}$) with Co$K\alpha$ radiation [4, 5]. The combination of peaks chosen for the analysis was $(2\,1\,1)_\alpha$, $(2\,2\,0)_\gamma$ and $(3\,1\,1)_\gamma$ [5]. The instrument was a differential transformer type of dilatometer with a maximum resolution of $3.5\,\mu$m. Tempering survey runs with continuous heating were carried out under vacuum at a controlled rate of $0.008\,\mathrm{K\,sec^{-1}}$. The specimen temperature was measured using a chromel–alumel thermocouple wire spark-welded to the centre of the test specimen face. The test specimens were 5 mm diameter by 80 ± 0.025 mm long rods with the ends accurately ground to the contour of a 100 mm diameter sphere.

The decomposition of austenite in the second stage and that of martensite in the third stage during the tempering reaction of high-carbon steel clearly overlap during the dilatometric measurements. It is therefore necessary to isolate the effect of overlap of the second and third stages in tempering. So, true changes of length caused by the decomposition of austenite and martensite were evaluated with the technique suggested by Averbach and Cohen [6]. An outline of the technique is described below. For the specimen lengths $\Delta L_1/L_1$ and $\Delta L_2/L_2$ of a pair of test specimens, 1 and 2, with different but known quantities of martensite and retained austenite, schematically shown in Fig. 1, their summation may be expressed by

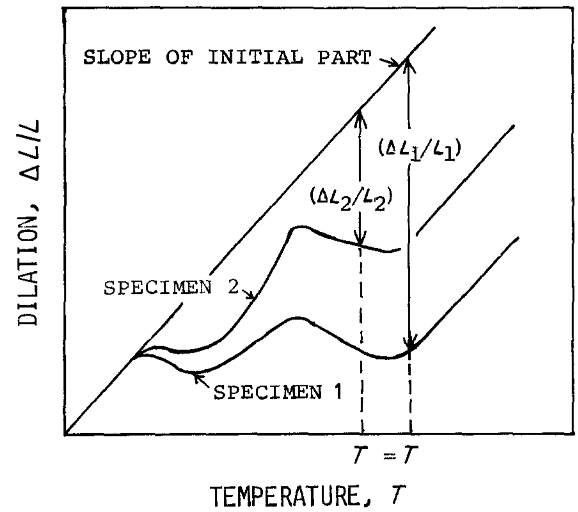

Figure 1 Schematic diagram of unit length changes in dilation curves during continuous heating.

$$\Delta L_1/L_1 = a_1 A + m_1 M \qquad a_1 + m_1 = 100\% \tag{9}$$

$$\Delta L_2/L_2 = a_2 A + m_2 M \qquad a_2 + m_2 = 100\% \tag{10}$$

where $\Delta L_1/L_1$ and $\Delta L_2/L_2$ are, respectively, the unit changes in length of Specimens 1 and 2 at a given temperature T (Fig. 1). A and M are the length changes caused by partial decomposition in 1% of the retained austenite and martensite, respectively, at a given temperature T. a_1 and a_2 are, respectively, the volume fractions of retained austenite in Specimens 1 and 2 before the test. m_1 and m_2 are, respectively, the volume fractions of martensite in Specimens 1 and 2 before the test. Solving Equations 9 and 10 for A and M, we obtain

$$100A = 100\left[m_2\left(\frac{\Delta L_1}{L_1}\right) - m_1\left(\frac{\Delta L_2}{L_2}\right)\right] \bigg/ (a_1 m_2 - a_2 m_1) \tag{11}$$

and

$$100M = 100\left[a_2\left(\frac{\Delta L_1}{L_1}\right) - a_1\left(\frac{\Delta L_2}{L_2}\right)\right] \bigg/ (a_2 m_1 - a_1 m_2) \tag{12}$$

$100A$ and $100M$ are the specimen lengths that would

TABLE II Heat treatment and quantities of retained austenite of test specimens

Designation of specimen	Austenitizing condition (K(k sec))	Quenching medium	Retained austenite (vol %)	
			As-quenched	Quench followed by treatment at 77 K
A	1133 (3.6)	Water	13.0	3.4
B	1133 (3.6)	Water	12.9	3.2
C	1133 (3.6)	Water	12.8	3.2

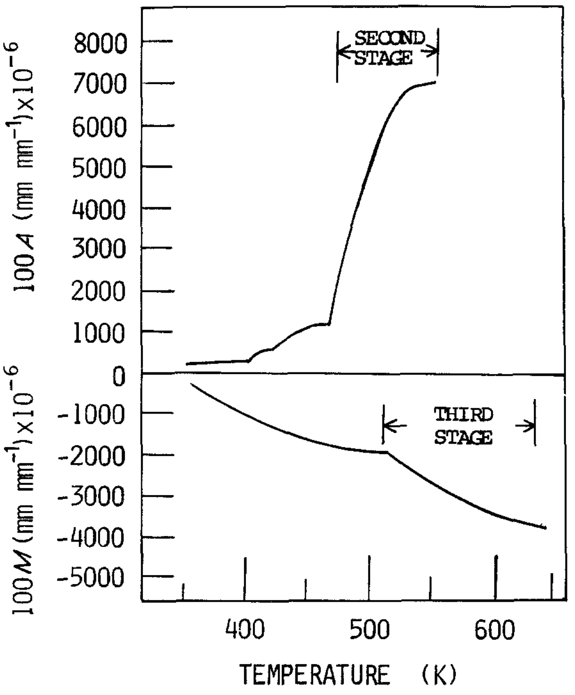

Figure 2 Curves plotting 100% retained austenite (100*A*) or 100% martensite (100*M*) against temperature in Specimen A (heating rate 0.008 K sec^{-1}).

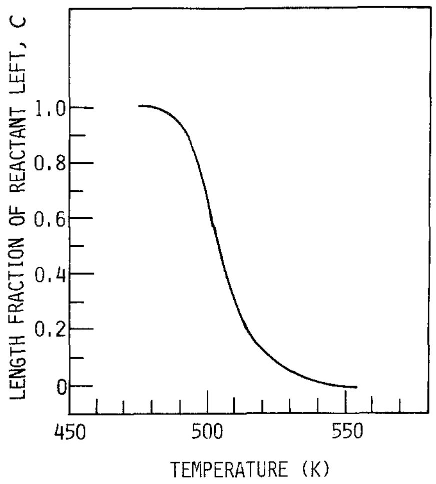

Figure 3 Curve plotting length fraction of reactant left, *C*, against temperature *T*, for the second stage (473 to 553 K) of the tempering reaction of Specimen A (heating rate 0.008 K sec^{-1}).

occur at temperature T in a hypothetical specimen of 100% retained austenite and 100% martensite, respectively. Thus, 100A and 100M are used as the specimen length, $\Delta L/L$, in the decomposition of retained austenite and martensite, respectively.

Fig. 2 shows the curves of 100A and 100M plotted as a function of temperature T, for Specimen A. It shows the range of the second and third stages in tempering of the steel. This is based on the following three assumptions: (i) the second stage is the temperature range where rapid expansion appears in the curve of 100A against temperature; (ii) the third stage is the temperature range where the second-step contraction appears in the curve of 100M against temperature, while the first-step contraction is the first stage in the tempering reaction; and (iii) the temperature at which the second or third stage is completed is defined as the temperature at which the expansion or contraction is saturated in the dilatometric curve.

Figs 3 and 4 are traces of the length fraction of reactant left, C, against the temperature T for Specimen A, derived on the basis of data shown in Fig. 2. The activation energy and frequency factor were obtained from the temperature, slope and length fraction of reactant left at the inflection point of the curves. The results are shown along with those for Specimens B and C in Table III. The inflection point and slope of the curve should be evaluated with significant precision and rapidity through various techniques, for which a computer is ideally suited. Hence, they were evaluated by means of a graphical solution using a half-silvered mirror, which is one of the potential techniques which can be readily used [7]. The outline of the technique is as follows: first, (i) a normal XY at each point on the curve plotting length fraction of reactant left, C, against temperature, T, is drawn by turning the silvered mirror M on Point P (Fig. 5) to put an image of the curve AP, A′P, on to a part of the curve, PB, opposite to the mirror. Then, (ii) the tangent $\mathrm{d}C/\mathrm{d}T$ at the point is calculated from the slope of the normal. Finally, (iii) the inflection slope $(\mathrm{d}C/\mathrm{d}T)_i$, and point ($T_i$ and C_i) are determined by measuring the maximum value of $\mathrm{d}C/\mathrm{d}T$ and its point on the curve plotting $\mathrm{d}C/\mathrm{d}T$ against T, respectively.

The activation energy and frequency factor were calculated from Equations 7 and 8, respectively, ($n = 1$), because both the second and third stages in the tempering reaction appear to obey first-order kinetics when changes in the specimen length are measured during continuous heating [8]. This could be due to the fact that when changes in the specimen length are measured on continuous heating, the effect

TABLE III Kinetic parameters of the second and third stages in the tempering reaction of 0.94% C plain carbon steel calculated using Equations 7 and 8 (heating rate Φ = 0.008 K sec^{-1})*

Designation of specimen	Stage of tempering	T_i (K)	C_i	$(\mathrm{d}C/\mathrm{d}T)_i$ (K^{-1})	Activation energy, E (kJ mol^{-1})	Frequency factor, Z
A	Second	507	0.38	-3.11×10^{-2}	174.82	6.86×10^{14}
	Third	572	0.37	-1.08×10^{-2}	79.36	4.16×10^{3}
B	Second	506	0.37	-3.08×10^{-2}	177.11	3.13×10^{14}
	Third	573	0.39	-1.17×10^{-2}	81.86	7.39×10^{3}
C	Second	506	0.37	-3.05×10^{-2}	175.39	8.59×10^{14}
	Third	573	0.39	-1.13×10^{-2}	79.05	3.77×10^{3}

*R = 8.31 J mol^{-1} K^{-1}.

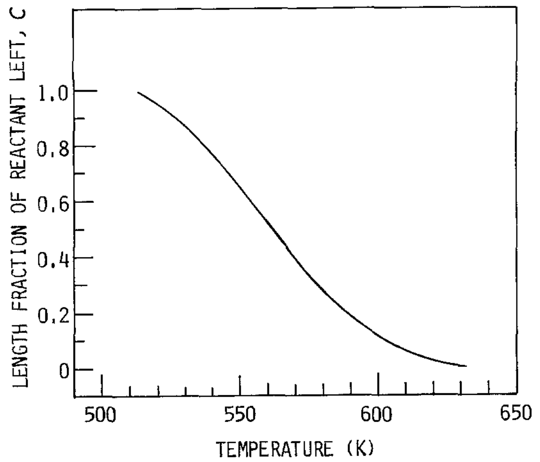

Figure 4 Curve plotting length fraction of reactant left, *C*, against temperature *T*, for the third stage (513 to 633 K) of the tempering reaction of Specimen A (heating rate 0.008 K sec^{-1}).

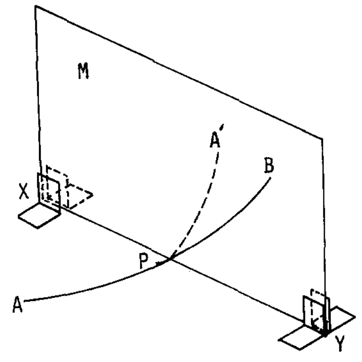

Figure 5 Technique for drawing normal to curve using half-silvered mirror.

of stress relief is not apparent in the second and third stages because it emerges between the first and second stages in the tempering [9]. As can be seen from the results, the activation energy E ranges from 174.82 to 177.11 kJ mol^{-1} for the second stage in the tempering reaction and from 79.05 to 81.85 kJ mol^{-1} for the third stage. For the activation energy of the second stage, a similarity in magnitude with the activation energy of carbon diffusion in austenite is observed [10]. The activation energy of the third stage is in good agreement with that of carbon diffusion in α-iron obtained by Wert [11].

These values fit those obtained by the earlier workers who obtained their estimates by detailed studies of isothermal tempering survey runs at several temperatures [1–3]. However, the natural question arises as to whether the kinetic parameters calculated using the present equations can be applied to an entire curve. Therefore, in order to clarify this, the calculated length fractions of reactant left, C, at various temperatures for the second and third stages of Specimen A were evaluated using Equation 13 below, modified from Equation 5, as shown in Tables IV and V. The results were then compared with the experimental curves in Fig. 3 and 4 (Fig. 6).

$$C = -\left(\frac{\mathrm{d}C}{\mathrm{d}T}\right)\frac{\Phi}{Z}\exp\left(\frac{E}{RT}\right) \qquad (13)$$

It appears from this figure that the calculated C points could be put on the experimental curve independent of the second and third stages in tempering. This result shows that the kinetic parameters evaluated by the present approach can apply to not only the vicinity of the inflection point of the curve, but also nearly the whole curve.

Although the heating rate Φ does not appear directly in Equation 7, it is an important factor for accurate estimation of the rate constants of the second and third stages in the tempering reaction. Thus, the effect of the heating rate on the kinetic parameters was investigated using Specimen A. The result demonstrated that the heating rate should not exceed 0.016 K sec^{-1}. This is due to the fact that the inflection temperature becomes high abruptly when the heating rate is over 0.016 K sec^{-1}. From the above results, it is

TABLE IV Calculated values of length fraction of reactant left, *C*, at various temperatures for the second stage in the tempering of Specimen A, calculated from the curve in Fig. 3 and Equation 13 (Φ = 0.008 K sec^{-1})

Temperature, T (K)	dC/dT (K^{-1})	Activation energy, E (kJ mol^{-1})	Frequency factor, Z	Calculated length fraction of reactant left, C
495	-2.60×10^{-2}	174.82	6.86×10^{14}	0.86
499	-2.97×10^{-2}	174.82	6.86×10^{14}	0.71
503	-3.05×10^{-2}	174.82	6.86×10^{14}	0.52
507	-3.11×10^{-2}	174.82	6.86×10^{14}	0.38
512	-2.94×10^{-2}	174.82	6.86×10^{14}	0.24
523	-2.62×10^{-2}	174.82	6.86×10^{14}	0.10

TABLE V Calculated values of length fraction of reactant left, *C*, at various temperatures for the third stage of Specimen A, calculated from the curve in Fig. 4 and Equation 13 (Φ = 0.008 K sec^{-1})

Temperature, T (K)	dC/dT	Activation energy, E (kJ mol^{-1})	Frequency factor, Z	Calculated length fraction of reactant left, C
520	-0.50×10^{-2}	79.36	4.16×10^{3}	0.90
540	-0.81×10^{-2}	79.36	4.16×10^{3}	0.75
560	-1.04×10^{-2}	79.36	4.16×10^{3}	0.51
573	-1.08×10^{-2}	79.36	4.16×10^{3}	0.37
590	-0.92×10^{-2}	79.36	4.16×10^{3}	0.19
600	-0.64×10^{-2}	79.36	4.16×10^{3}	0.10

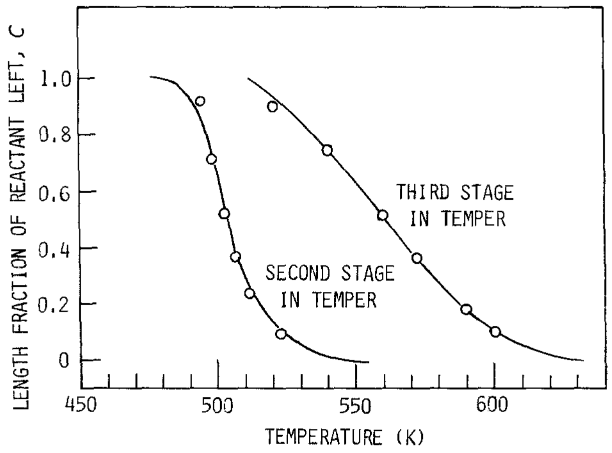

Figure 6 (———) Exerimental curves for the second and third stages in the tempering of Specimen A (heating rate 0.008 K sec^{-1}) and (O) calculated length fraction of reactant left, *C*, at various temperatures calculated by Equation 13.

found that the new equations derived from this study enable one to rapidly determine the kinetic parameters of a non-reversible reaction from non-isothermal dilatometric curves. However, further studies are needed with more materials before complete normalization of this analysis can be verified. This aspect is currently in progress and will be reported in future work.

4. Conclusions

New equations derived from this study enable one to rapidly determine the kinetic parameters of a non-reversible reaction from non-isothermal dilatometric curves. The main advantages of the proposed approach are considerable economies in experimental procedure and the avoidance of experimental errors associated with the onset of reactions before isothermal conditions are attained. The temperature, slope and length fraction of reactant left at the inflection point in the curve plotting the length fraction of reactant left against the temperature gave the activation energy and frequency factor of the reaction. The good agreement between values of activation energy obtained by the new equations and reported literature values for the second and third stages in the tempering of plain carbon steel served to validate this new approach. It was further demonstrated that the kinetic parameters evaluated by the present equations can apply to not only the inflection point of the curve, but also nearly the whole curve.

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