Quantification of evolution of multiple simultaneous phase transformations using dilation curve analysis (DCA)

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A novel mathematical approach for the independent quantification of phase fractions in multiple simultaneous phase transformations is introduced. The proposed dilation curve analysis is very general, relying only on raw dilatation data and the density of some of the constituents involved in the transformations. Transformation start and end temperatures and instantaneous phase fractions are accurately measured using this method. As an example, the simultaneous transformation of austenite to bainite and martensite in seven cylindrical AISI 4140 steel samples cooled at rates between 1 and 4 K/s from 1223 K (950 °C) is used to show the feasibility of this new methodology. The martensite and bainite fractions calculated using the presented methodology for all seven samples are in good agreement with the ones measured with quantitative metallography. Hot stage microscopy was also performed on a sample of the same batch, yielding quantitative results consistent with the start temperatures from the analysis proposed.

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1. Introduction

Dilatometry is a well-established technique primarily used to study the response of a material to temperature change [1]. A dilatometer records the length changes that occur during the heat treatment of a sample. The relative change in length as a function of temperature data obtained from a dilatometer can then be studied to determine if the sample experienced any phase transformation(s) during the heat treatment [2]. The raw data can also be used to calculate the start and finish temperatures of the transformation(s). American Society for Testing and Materials (ASTM) has developed a well-known method (typically called the lever-rule method) for quantifying the fraction of a forming constituent from dilatation data [3]. The ASTM method assumes the progression of the phase transformation is proportional to the dilatation progression between two baselines [4]. This method can only be applied to single phase transformation, or to multiple phase transformations if they can be considered to be in sequence with no overlaps. This is rarely the case in most materials, specifically steels continuously cooled after austenitizing [5]. The shortcomings of the ASTM method are studied in Ref. [6]. This lack of quantification of the fractions of constituents is especially obvious in the continuous cooling transformation (CCT) and time-temperature-transformation (TTT) diagrams of [7] and [8].

Among previous work in the quantification of simultaneous phase transformations is the pioneering research of Onink et al. on unalloyed steels [9]. Their models are based on the lattice parameters of the constituting phases and their dependence on temperature and composition. Many researchers have built on the models presented in Ref. [9] and tried to expand them to take into account alloying elements [10–12], and diffusionless phase transformations (e.g. formation of martensite from austenite) [5,13–15]. Andres et al. have developed a model on the basis of lattice parameters for the decomposition of pearlite to austenite in an eutectoid steel upon heating [16]. Other researchers have taken a different approach and used the density of the constituting phases as the basis of their models [4,17]. Dkhuijen et al. have developed a self-calibrating method with expressions for the phase densities as a function of temperature and composition to predict the austenite fraction in austenitization of a low carbon steel [18]. Avrami-type transformation models are also used in some literature to
quantify the transformation kinetics in low carbon steels [19,20].

All of the models presented in the previous paragraph are finely tuned for specific alloy systems (mainly low alloy, low carbon steels) and are rarely applicable to the broader group of materials. In addition, most of the models suffer from limiting assumptions (e.g. geometrical assumptions, equilibrium estimations for nonequilibrium transformations, limited number of alloying elements, etc.) that hinder their application to all phase transformations.

Besides dilatometry, alternate techniques of measuring phase fractions also exist. Direct measurement techniques include microscopy [21], differential scanning calorimetry (DSC) [21–24], differential thermal analysis (DTA) [25,26], synchrotron diffraction [27]. All of these techniques are either slow, expensive or difficult to access, and in some cases, unable to accommodate realistic sample sizes or cooling rates. Indirect measurement techniques include electrical resistivity [28–30]. These techniques yield data in a format analogous to dilatometry, and it is likely the techniques presented here could also be extended to resistivity measurements. Research in the field of cooling curve analysis has led to the development of a promising methodology, independent of the type of material, to distinguish individual phase fractions in multiple simultaneous phase transformations [31–33]. Recently, a new approach to quantifying constituent fractions from dilatation data for single phase transformations was developed by Ref. [34]. This method is referred to as dilation curve analysis (DCA) and was compared to cooling curve analysis (CCA) results for an austenite to martensite single phase transformation in 9Cr3W3CoVNb steel. CCA has proven to be effective at producing similar results to dilatometry despite its drastically simpler experimental setup [34].

The aim of this paper is to present a novel mathematical formulation to be able to extract individual phase fractions of a multi-step phase transformation from the dilation curve. The multiple phase transformations can be simultaneous or consecutive. The highlight of this methodology is that it requires minimum input data from the user regarding the phase transformations. The presented methodology allows for its application to almost any material with very few assumptions and little user interaction.

2. Dilation curve analysis (DCA) during multiple transformations

The proposed DCA methodology consists of presenting all terms affecting the change in length with temperature in one single equation. The temperature dependent terms are then separated from the terms that depend on phase fraction. Raw dilatometry data and specific physical properties of some of the constituents (explained in more detail later on) are then used to determine values for the temperature dependent terms. Finally, the equations are solved independently to obtain all phase fractions as a function of temperature (i.e. phase fraction curves).

Without loss of generality, consider an isotropic \( n \)-constituent system with a sequence of phase transformations \( 1 \rightarrow 2, 1 \rightarrow 3, \ldots, 1 \rightarrow n \) taking place at different time scales during cooling or heating with Constituent 1 being the only parent phase. The type and number of phase transformations do not affect the application of the proposed methodology i.e. the phase transformations can be sequential, simultaneous, or nested. The development of the methodology presented here will focus on nested phase transformations (one within the other) which are the most complicated to separate. Consider a sample in which the microstructure is made of constituents \( 1, 2, \ldots, i, \ldots, n \). For the case of nested transformations, \( n = 1 \) refers to the original parent constituent (typically austenite for the case of steels during cooling). Each constituent can be a phase (e.g. martensite) or a mixture of phases (e.g. bainite). The total volume of the sample is given by the volume of all constituents:

\[
V_T = \sum_{i=1}^{n} V_i
\]

where \( V_T \) is the total volume of the sample and \( V_i \) is the volume of constituent \( i \). The constituent volumes \( (V_i) \) can be calculated from their mass fraction and density \( (V_i = m_i / \rho_i) \), where \( m_i \) is the mass fraction of constituent \( i \), \( m_i = m_{fi} / \rho_i \) is the density of constituent \( i \) and \( m_T \) is the total mass of the sample. The nomenclature used throughout this paper is described in Table 1. Applying these considerations to Equation (1) results in:

\[
V_T = \sum_{i=1}^{n} f_i \rho_i
\]

This equation accounts for multiple constituents present at any given temperature, with those that are not present having a mass fraction \( (f_i) \) of zero. For example, the experiments discussed later use the three constituent system of austenite, bainite, martensite (\( n = 3 \)) where \( i = 1 \) is assigned to austenite, \( i = 2 \) is for bainite, and \( i = 3 \) is assigned to martensite. The total mass of the sample in Equation (2) can be represented by the initial density and volume of the sample as \( m_T = \rho_0 V_0 \). For each of the product constituents (i.e. \( i \geq 2 \)), the term \( f_i \) can be split up into a temperature dependent variable \( (f_i^t) \) and a constant \( (f_i^c) \). \( f_i^t \) for each of the product constituents ranges from 0, before the transformation, to 1, after the transformation is complete. \( f_i^c \) is defined only for the transformation product constituents and is the final mass fraction of constituent \( i \) after the transformation is complete. \( f_i^t \) can be confirmed through microscopy after the transformation is complete. Hence, \( f_i = f_i^t f_i^c \).

To quantify the progression of constituents as a function of temperature, it is useful to create a differential equation by differentiating Equation (2) with respect to temperature to obtain:

<p>| Table 1 |
| List of terms and symbols used. |</p>
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>Sample cross-sectional area</td>
<td>( \mu m^2 )</td>
</tr>
<tr>
<td>( C_i )</td>
<td>Quantity defined in Equation (4)</td>
<td>( \mu m )</td>
</tr>
<tr>
<td>( f_i )</td>
<td>Actual mass fraction of constituent ( i )</td>
<td>( g/g )</td>
</tr>
<tr>
<td>( f_i^c )</td>
<td>Final mass fraction of constituent ( i )</td>
<td>( g/g )</td>
</tr>
<tr>
<td>( f_i^t )</td>
<td>Normalized mass fraction of constituent ( i )</td>
<td>( g/g )</td>
</tr>
<tr>
<td>( L )</td>
<td>Length of the sample</td>
<td>( \mu m )</td>
</tr>
<tr>
<td>( L_0 )</td>
<td>Initial length of the sample</td>
<td>( \mu m )</td>
</tr>
<tr>
<td>( m_i )</td>
<td>Mass of constituent ( i )</td>
<td>( g )</td>
</tr>
<tr>
<td>( m_T )</td>
<td>Total mass of the sample</td>
<td>( g )</td>
</tr>
<tr>
<td>( n )</td>
<td>Index number</td>
<td>( _ )</td>
</tr>
<tr>
<td>( T_i )</td>
<td>( i )th constituent formation start temperature</td>
<td>( s )</td>
</tr>
<tr>
<td>( T_f )</td>
<td>( i )th constituent formation finish temperature</td>
<td>( s )</td>
</tr>
<tr>
<td>( T )</td>
<td>Measured temperature of the sample</td>
<td>( K )</td>
</tr>
<tr>
<td>( V_0 )</td>
<td>Initial volume of the sample</td>
<td>( \mu m^3 )</td>
</tr>
<tr>
<td>( V_i )</td>
<td>Volume of constituent ( i )</td>
<td>( \mu m^3 )</td>
</tr>
<tr>
<td>( V_T )</td>
<td>Total volume of the sample</td>
<td>( \mu m^3 )</td>
</tr>
<tr>
<td>( \rho_i )</td>
<td>Linear thermal expansion coefficient of constituent ( i )</td>
<td>( 1/K )</td>
</tr>
<tr>
<td>( \rho_i )</td>
<td>Volumetric thermal expansion coefficient of constituent ( i )</td>
<td>( 1/K )</td>
</tr>
<tr>
<td>( \varepsilon_T )</td>
<td>Average linear thermal expansion coefficient of constituent ( i )</td>
<td>( 1/K )</td>
</tr>
<tr>
<td>( \gamma_T )</td>
<td>Total strain due to change in temperature</td>
<td>( \mu m/\mu m )</td>
</tr>
<tr>
<td>( \gamma_e )</td>
<td>Quantity used in Equation (6)</td>
<td>( \mu m/K )</td>
</tr>
<tr>
<td>( \xi_e )</td>
<td>Quantity used in Equation (3)</td>
<td>( \mu m/K )</td>
</tr>
<tr>
<td>( \xi_i )</td>
<td>Quantity related to specific length used in Equation (4)</td>
<td>( \mu m/K )</td>
</tr>
<tr>
<td>( \rho_0 )</td>
<td>Initial density of the sample</td>
<td>( g/\mu m^3 )</td>
</tr>
<tr>
<td>( \rho_i )</td>
<td>Specific density of constituent ( i )</td>
<td>( g/\mu m^3 )</td>
</tr>
</tbody>
</table>
\[ \frac{1}{V_0} \frac{dV}{dT} = \sum_{i=1}^{n} \left( f_i \frac{\partial f_i}{\partial T} + \lambda_i \frac{df_i}{dT} \right) \]

(3)

where \( \lambda_i \equiv \rho_i \beta_i \) and it can be shown that \( \partial \lambda_i / \partial T = 3 \lambda_i \alpha_i \) with \( \alpha_i \) being the instantaneous linear thermal expansion coefficient of constituent \( i \) (i.e. \( \alpha_i = \frac{1}{L_t} \frac{dL}{dT} \)) where \( L_t \) is a generic length for constituent \( i \). The summation of all mass fractions adds to unity: \( \sum_{i=1}^{n} f_i = 1 \). Constituent 1 is the only constituent in the parent microstructure so, \( f_1 = 1 \). Also, for the type of nested transformations considered as an example above, \( \sum_{i=2}^{n} f_i = 1 \). In this case the summation starts at \( i = 2 \) since the parent constituent should not be included among the transformation products. Equation (3) can be rearranged considering the relationship between linear and volumetric thermal expansion coefficients (i.e. \( \beta = 3 \alpha \) where \( \beta \equiv \frac{1}{V_t} \frac{dV}{dT} \)) which will yield \( \frac{dV}{dT} = \frac{3V}{V_t} \frac{dV}{dT} \). For isotropic materials the ratio \( V/V_0 = (L/L_0)^3 \):

\[ 3 \left( \frac{L}{L_0} \right)^2 \frac{2}{L_0} \frac{dL}{dT} = \sum_{i=1}^{n} \left( 3f_i^2 \lambda_i \alpha_i + \lambda_i \frac{df_i}{dT} \right) \]

(4)

where \( L_0 \) is the initial length of the sample. For a typical material, the factor \( (L/L_0)^2 \) is very close to unity. The error caused by approximating \( (L/L_0)^2 \) as unity is discussed in the Appendix. Equation (4) can then be rearranged as:

\[ \frac{dL}{dT} = L_1 + \sum_{i=2}^{n} \left( L_i f_i^2 \right) + C_{\lambda_i} \frac{df_i}{dT} \]

(5)

The terms related to Constituent 2 (bainite in the experiments performed) can be isolated by rearranging Equation (5) as:

\[ \frac{dL}{dT} = \gamma_2 + L_2 f_2^2 + C_{L_2} \frac{df_2}{dT} \]

(6)

where \( \gamma_2 \equiv C_1 + \sum_{j=3}^{n-1} \left( L_i f_i^2 + C_{L_i} \frac{df_i}{dT} \right) \). The convenience of this rearrangement is that \( \gamma_2 \) does not depend on the evolution of Constituent 2. For isolating the terms related to constituent \( i \), the equivalent of Equation (6) is \( dL/dT = \gamma_i + L_i f_i^2 + C_{L_i} \frac{df_i}{dT} \) where \( \gamma_i \equiv C_1 + \sum_{j=2}^{n-1} \left( L_i f_i^2 + C_{L_i} \frac{df_i}{dT} \right) \).

Every \( L_i \) and \( \gamma_i \) can be calculated by fitting a baseline to a specific portion of the derivative of the dilatation data obtained from a dilatometry experiment. \( L_1 \) represents the sample material before any transformation has started (i.e. the portion of the dilatation curve above \( T_{S1} \) in Fig. 1(a)). Therefore, we can evaluate \( L_1 \) by fitting a function (a linear fit is sufficient in most cases) to the portion of the derivative of the dilatation curve that only consists of Constituent 1 (austenite in the experiments performed). The condition under which \( L_1 \) can be tracked using a linear fitting is discussed in the Appendix section. This approach to evaluating \( L_1 \) does not require explicit evaluation of the individual parameters that make up \( L_1 \), i.e. \( L_0, \rho_0, \rho_1, \alpha_1 \). When the only constituent present in the material is Constituent 1, all the other phase fractions will be zero \( (f_2 = \ldots = f_n = 0) \) in Equation (6): \( dL/dT = L_1 \).

A similar approach can be used to evaluate each \( L_i \) and \( \gamma_i \). From a specific portion of the derivative of the dilatation curve, Equation (7) demonstrates how each portion of the derivative of the dilatation curve in Fig. 1 is used to evaluate \( L_i \) and \( \gamma_i \).

\[
\begin{align*}
L_1 & \quad \text{eval. from above only Constituent 1 is present(above } T_{S2}) \\
L_2 & \quad \gamma_2 \quad \text{eval. from during the conditions after Constituent 2 finishes forming(below } T_{F2}) \\
\gamma_2 & \quad \text{eval. from during the conditions before Constituent 2 has formed (above } T_{S2}) \\
L_n & \quad \gamma_n \quad \text{eval. from during the conditions after Constituent n finishes forming (below } T_{F_n}) \\
\gamma_n & \quad \text{eval. from during the conditions before Constituent n has formed (above } T_{S_n})
\end{align*}
\]

(7)

where \( L_1 \equiv \rho_1 \alpha_1 \), \( L_i \equiv \rho_i \alpha_i \left( \lambda_i \alpha_i - 1 \right) \) for \( i \neq 1 \), and \( C_{\lambda_i} \equiv \rho_i \alpha_i \left( \lambda_i - 1 \right) / 3 \). The definition of \( L_i \) at this stage is to gather all the terms related to constituent \( i \) in a single parameter that can be tracked when fitting to experimental data discussed later.

For typical materials, \( \lambda_i - 1 \) is much smaller than either \( \lambda_1 \) or \( \lambda_i \) and \( C_\lambda \) is considered as independent of temperature. The conditions under which \( C_\lambda \) is constant are established in the Appendix section. A similar relationship can be established between every \( L_i \) and \( \alpha_i \) where \( L_i \) will be proportional to the difference between the linear thermal expansion coefficient of constituent \( i \) and Constituent 1.

The linear thermal expansion of the associated constituents and is nearly constant in most materials. This temperature dependence can be captured as a gentle slope in a graph of \( dL/dT \) versus temperature. Fig. 1(b) schematically shows how the values in Equation (7) are fitted to the derivative of the dilation curve. \( C_{\lambda_i} \) is determined by iteration. The iterations are run until the value of \( f_i^* = 1 \) when constituent \( i \) has finished forming (i.e. below \( T_{F_i} \)). Typically 2 to 4 iterations are enough and for the case of austenite decomposition, a good starting value for the iterations is \( C_{\lambda_i} = 10 \mu m \) for a sample of 10 mm length.
After evaluating $L_i$ and $C_i$, an Euler explicit integration scheme is applied to Equation (6), and similar equations for all other constituents, to numerically calculate the fraction of each constituent starting from an initial condition of $f_i^C = 0$. The phase fraction for constituent $i$ will be:

$$f_i^{j+1} = f_i^{j} + \left[\frac{T_{j+1} - T_j}{C_i}\right] \left[\frac{T_{j+1} - L_j}{T_{j+1} - T_j} - \gamma_i - C_i f_i^C\right]$$  \hspace{1cm} (9)

The characteristic mass fraction of constituent $i$ can be calculated using the definition of $C_i$:

$$f_i^C = \frac{3C_i}{L_0(\lambda_1 - \lambda_2)}$$  \hspace{1cm} (10)

The initial length and initial density of the sample used for this analysis along with the density of Constituent 1 and $n-2$ other constituents are needed to calculate constituent fractions (e.g. in the case of the experiments performed here, only the density of austenite and martensite are required). The initial length of the sample is typically measured for every dilatometry experiment. The density of most constituents can be looked up from standard thermophysical tables, calculated through Thermo-Calc software [35] or experimentally measured using the displacement method [36]. The final outcome of the proposed methodology is separated fraction curves for each of the constituents as shown in Fig. 1(c).

3. Case study

The transformation of austenite to bainite and martensite upon cooling is used as an example to show the application of the proposed methodology. In this example the system consists of 3 constituents, austenite, bainite, martensite ($n = 3$) where $i = 1$ is assigned to austenite, $i = 2$ is for bainite, and $i = 3$ is assigned to martensite. Seven AISI 4140 steel samples with the composition shown in Table 2 were cooled at different rates to form various fractions of bainite and martensite. The cooling rates were chosen

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Cu</th>
<th>P</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount</td>
<td>0.41</td>
<td>0.73</td>
<td>0.82</td>
<td>0.17</td>
<td>0.06</td>
<td>0.13</td>
<td>0.011</td>
<td>0.022</td>
</tr>
</tbody>
</table>

* Nominal value of carbon in AISI 4140 steel.
in a way that no pro-eutectoid ferrite would form upon cooling. The bainite and martensite fractions were calculated using the proposed methodology and compared to those obtained from metallography. Hot-stage microscopy was also performed on a high temperature confocal scanning laser microscope (CSLM) to confirm the simultaneous formation of bainite and martensite from austenite. The composition of the AISI 4140 steel was measured with ICP-MS.

Cylindrical dilatometry samples were machined to size from a bar of AISI 4140 steel using a mini-lathe. The sample length, diameter, mass and target cooling rate are reported in Table 3. For the cooling rates chosen, the temperature control system in the dilatometer always kept a closed-feedback loop close to the target temperature.

K-type thermocouples (0.38 mm in diameter) were spot welded to the samples using a DCC Corp. Hotspot TC welder. For the dilatometry investigation, a vertical Linseis RITA L78 high speed quenching dilatometer was utilized. The dilatometry heating and cooling cycle is characterized by a heating rate of 10 K/s, a peak temperature of 1223 K (950°C), a holding time of 30 s, and different cooling rates as shown in Table 3 to room temperature. The change in the length of the samples with temperature is precisely recorded by the dilatometer. Upon cooling, austenite will first transform to bainite and the remaining austenite will then transform to martensite while the bainite is evolving [37–39]; therefore, only the cooling portion of the experimental data is relevant to the current methodology. As an example, the resulting change in length with temperature upon cooling for sample 3 (cooled at 2 K/s) is shown in Fig. 2.

Fig. 3 displays a room temperature optical micrograph of the microstructure of the AISI 4140 steel sample cooled at 2 K/s at 1000 times magnification. The sample was polished and etched using 5% Nital solution to reveal the microconstituents. The microstructure consists of bainite and martensite with the white phase being martensite and the darker constituent showing bainite.

### 3.1. Determination of bainite and martensite fractions

The \( L_i \) and \( \gamma_i \) for each of the samples are calculated by fitting a line to the appropriate section of the derivative of the dilation curve. As an example, the fitting of the values in Equation (7) to the experimental data in sample 3 (cooled at 2 K/s) is shown in Fig. 4. The differential curve shown in Fig. 4 was obtained by using Newton's difference quotient by taking the ratio of the difference in change in length between subsequent time steps to the difference in temperature for the same time step (i.e. \( \frac{L_2 - L_1}{T_2 - T_1} \)). Also, a 25 point moving average smoothing process was used to plot the derivative curve. Points A and B in Fig. 4 were chosen in a way that the line passing through these two points is the best approximation for the entire region where only austenite exists. Similarly, the line passing through points C and D in Fig. 4 is the best fit line to approximate the dependence of \( \gamma_2 \) with temperature. The dilation curve in the experimental case studied here (austenite to bainite and martensite transformation) shows fewer deflections as compared to the schematic in Fig. 1. This is because bainite and martensite finish forming at the same time. Therefore, a single line passing through points E and F in Fig. 4 can be used to simultaneously show the dependence of \( L_2 + \gamma_2 \) and \( L_3 + \gamma_3 \) on the temperature.

### Table 3

Dimensions, weight and target cooling rate of dilatometry samples used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Target cooling rate (K/s)</th>
<th>Length (mm)</th>
<th>Diameter ±0.01 (mm)</th>
<th>Mass ±0.01 (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>8.26</td>
<td>4.95</td>
<td>1.27</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>8.07</td>
<td>4.95</td>
<td>1.24</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>7.73</td>
<td>4.95</td>
<td>1.19</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>7.77</td>
<td>4.95</td>
<td>1.19</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>8.08</td>
<td>4.95</td>
<td>1.24</td>
</tr>
<tr>
<td>6</td>
<td>3.5</td>
<td>7.58</td>
<td>4.95</td>
<td>1.16</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>9.54</td>
<td>4.95</td>
<td>1.46</td>
</tr>
</tbody>
</table>
As an example, the values for the fitted parameters for sample 3 are shown in Table 4. The phase fraction evolution curves for bainite and martensite were then calculated for all seven samples using the presented methodology. For example, the fraction curves for sample 3 are shown in Fig. 5 and Fig. 6. The formation of bainite and martensite are clearly marked on Fig. 5. The final phase fraction for this sample consists of 62% bainite and 38% martensite.

The bainite and martensite fractions obtained from the present methodology were verified by taking optical micrographs of the final microstructure of all seven samples. All seven samples were polished and etched with a 5% Nital solution for 8–10 s to reveal the microstructure. The fraction of bainite and martensite in each sample were calculated using area analysis by thresholding in ImageJ software [40]. Between four and eight optical micrographs at different magnifications (ranging from 5× to 1000× magnification) were analyzed using ImageJ to obtain the bainite and martensite fractions for each sample. It was presumed there is negligible amounts of retained austenite in the samples and hence, all the white constituent was associated to martensite and the darker constituent was assumed to be bainite. The average of phase fractions obtained from the analyzed micrographs per sample was used as the final fraction. 95% confidence interval of the analyzed micrographs is used as the error in the measurements. Table 5 summarizes the values of the bainite and martensite fractions obtained from both methods. The maximum difference between the fractions calculated using DCA and microscopy is 6.5% in sample 1.

### 3.2. Hot-stage microscopy

Hot-stage microscopy was conducted on a sample of the same steel cooled at 2 K/s to confirm the simultaneous formation of bainite and martensite from austenite. The bainite and martensite start temperatures ($B_s$ and $M_s$) were calculated from the hot-stage microscopy images by observing the first appearance of the new constituent. $B_s$ and $M_s$ values were compared to the values obtained from the current methodology for sample 3 considering the start as 1% of the total evolution of the transformation. Fig. 7 is a cascade of screen-shots from the corresponding transformation video obtained from the CSLM (included as Supplementary material). This figure shows the microstructure at $B_s$, $M_s$, and before and after bainite and martensite formation. The yellow and red arrows in these images respectively indicate the location of the forming bainite and martensite from austenite. The bainite and martensite start temperatures obtained from both methods for sample 3 are compared in Table 6. The difference in the martensite start temperature is much larger between the two methods than it is for the

### Table 4

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_1 - \gamma_2$</td>
<td>$2.349 \times 10^{-4} T + 0.169$</td>
<td>$\mu m/K$</td>
</tr>
<tr>
<td>$L_2 + \gamma_2 - L_3 + \gamma_3$</td>
<td>$1.102 \times 10^{-4} T + 0.196$</td>
<td>$\mu m/K$</td>
</tr>
<tr>
<td>$\gamma_3$</td>
<td>$-1.153 \times 10^{-3} T + 0.598$</td>
<td>$\mu m/K$</td>
</tr>
<tr>
<td>$C_{\text{1}}$</td>
<td>$2.554 \times 10^{-1}$</td>
<td>$\mu m$</td>
</tr>
<tr>
<td>$C_{\text{2}}$</td>
<td>$1.137 \times 10^{-1}$</td>
<td>$\mu m$</td>
</tr>
</tbody>
</table>

![Fig. 5. Bainite fraction versus temperature for AISI 4140 steel cooled at 2 K/s.](image1)

![Fig. 6. Martensite fraction versus temperature for AISI 4140 steel cooled at 2 K/s.](image2)
bainite start temperature. This is mainly due to the calibration of the measured temperature in the CSLM. The temperature measurements in the CSLM are not calibrated against reference materials at low temperatures (below approximately 300 °C). Instead, an extrapolation from high temperature calibration values is used to correct the measured temperatures at lower temperature.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.actamat.2015.09.025

4. Discussion

When fitting a curve to the derivative of the dilation curve, the authors found that a linear function is best suitable to capture each portion of the curve for the case of the current experimental setup. Further details about the curve fitting technique used in this methodology can be found in Ref. [34]. An exponential function can also be used to represent the different sections of the curves as

Table 5
Bainite and martensite fractions calculated using the present methodology and optical microscopy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cooling rate (K/s)</th>
<th>Bainite frac. from DCA</th>
<th>Martensite frac. from DCA</th>
<th>Bainite frac. metallography</th>
<th>Martensite frac. metallography</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.95</td>
<td>0.05</td>
<td>0.89 ± 0.07</td>
<td>0.11 ± 0.07</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>0.87</td>
<td>0.13</td>
<td>0.83 ± 0.09</td>
<td>0.17 ± 0.09</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0.62</td>
<td>0.38</td>
<td>0.61 ± 0.04</td>
<td>0.39 ± 0.04</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>0.29</td>
<td>0.71</td>
<td>0.32 ± 0.08</td>
<td>0.68 ± 0.08</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>0.09</td>
<td>0.91</td>
<td>0.07 ± 0.06</td>
<td>0.93 ± 0.06</td>
</tr>
<tr>
<td>6</td>
<td>3.5</td>
<td>0.05</td>
<td>0.95</td>
<td>0.04 ± 0.03</td>
<td>0.96 ± 0.03</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>0.002</td>
<td>0.998</td>
<td>0.009 ± 0.003</td>
<td>0.991 ± 0.003</td>
</tr>
</tbody>
</table>

Fig. 7. Cascade of hot-stage microscopy images before and after the bainite and martensite formation for sample 3 (cooled at 2 K/s). The yellow and red arrows in these images respectively indicate the location of the forming bainite and martensite from austenite. Full transformation video included as Supplementary Material (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 6
Comparison of the bainite and martensite start temperatures obtained from hot-stage microscopy and the current methodology for sample 3 (cooled at 2 K/s).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bs current method (°C)</th>
<th>Bs hot-stage microscopy (°C)</th>
<th>Ms current method (°C)</th>
<th>Ms hot-stage microscopy (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>503</td>
<td>508</td>
<td>305</td>
<td>274</td>
</tr>
</tbody>
</table>
suggested by Van Bohemen in Ref. [41]. This was carried out by the authors and was found that in the worst-case scenario the fitting results varied only 1.1% when an exponential function was used instead of a linear function. This shows that linear functions are much simpler and just as reliable as exponential functions to capture all the regions of the derivative of the dilatation curve for the current experimental setup.

Very small fluctuations in measured length are intrinsic to dilatometry even in an intended isothermal condition and when there is no phase transformation present. These variations result in slight oscillations in the calculated phase fractions with this methodology. For the experiments performed in this work, the amplitude of variations below 190 °C is of the order of 0.8% for bainite and 1.8% for martensite.

Detecting the initiation of the transformations in hot-stage microscopy is fairly simple. In contrast, identifying the end of the transformations is not possible. In the case of austenite transformation to bainite and martensite, the simultaneous formation of bainite and martensite in the sample used could not be confirmed or denied with hot-stage microscopy; although, there is enough evidence in the literature that for medium carbon steels, bainite can evolve below the $M_s$ temperature which has been confirmed with in situ simultaneous synchrotron X-ray diffraction and hot-stage microscopy [37–39].

The presented methodology can be used to build advanced continuous cooling transformation (CCT) diagrams. In the current state, CCT diagrams only display the start and finish temperatures for each of the constituent regions they contain. In some cases, the 50% transformation curve is estimated in some of the regions of the CCT diagrams. The current methodology can improve these CCT diagrams by adding “phase percent curves” to the diagrams in addition to the start and finish temperatures. This additional information can add value to classic CCT diagrams by providing the user with the amount of each constituent at each cooling rate. This can help metallurgists in many ways such as designing more accurate heat treatments and producing better welding procedures.

The methodology described in this paper should be applicable to any material in which phase transformations are well detected in a dilatometer. The proposed approach involves a modest amount of effort (e.g. calculating/finding the density of some constituents) that is different from previous methodologies; however, this extra effort allows for the proper accounting of phase fractions that is not possible otherwise. In addition, the effort spent on analyzing a specific alloy group does not need to be repeated for similar systems. By measuring the final phase fraction in unknown systems or systems which do not have reliable thermodynamic databases available, the density of all constituents involved in the transformations can be accurately back-calculated. This is an advantage over relying solely on available thermodynamic databases and can be used to get a deeper understanding of new or custom alloy systems.

The developed methodology can be used with any dilatation data which is obtained from dilatometry runs without having to change the experimental setup or applying any limiting assumptions. This methodology could likely be extended to isothermal transformations by modifying the starting equations to base them on time instead of temperature.

5. Conclusions

A rigorous mathematical model for the quantification of phase fractions in simultaneous phase transformations using dilatation data is introduced. The methodology was applied to AISI 4140 steel, and can potentially be extended to many other types of material. The outcome of this methodology is an accurate accounting of phase fractions as the transformations progress in continuous cooling for multiple simultaneous phase transformations.

Seven cylindrical AISI 4140 steel samples were austenitized and cooled to room temperature with constant cooling rates ranging from 1 to 4 K/s. The resulting microstructures consisted of different fractions of bainite and martensite. The martensite and bainite fractions calculated using the present method for all seven samples are in good agreement with that calculated through optical microscopy, with a maximum difference of 6.5% between the two methods. Hot-stage microscopy was performed on a high temperature confocal scanning laser microscope (CSLM). The bainite and martensite start temperatures ($B_s$ and $M_s$) from the current methodology were in good agreement with the values obtained from the CSLM. The results of these examples support the presented methodology as a tool capable of tracking multiple simultaneous phase transformations and amount of each constituent present in the material.

The proposed methodology can be used to better quantify all phase transformations. Specifically in steels, this methodology can help improve the quality of CCT diagrams by adding valuable information to these diagrams that could not be included with previous methods of analysis.

Acknowledgment

The authors would like to acknowledge Codes and Standards Training Institute (CASTI), MITACS and Natural Sciences and Engineering Research Council of Canada (NSERC) for their support of this work. Special gratitude to the Canadian Welding Association (CWA) for their support of this research through the CWA Edmonton graduate annual award for excellence in welding engineering.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.actamat.2015.09.025

Appendix

Determination of the density of martensite

The density of martensite cannot be determined using conventional equations based on the lattice parameters of martensite such as those presented in Ref. [42]; these theoretical equations for density of martensite only apply to iron–carbon binary alloys and do not take into account other alloying elements. The formulation for the lattice parameter of martensite given in Ref. [43] does not consider all the elements in the composition of the steel used in this experimental work. It assumes only iron atoms exist in the martensite unit cell, which is only an estimate for low alloy steels. In this work, the density of martensite in the AISI 4140 steel was experimentally measured using a sample of 100% martensite and the displacement method following the procedure stated in Ref. [36]. For the experimental calculation of martensite, the density of water at 295.6 K is 0.99778 g/cm$^3$ [36]. The density of austenite (required to calculate $f_s$) was estimated from dilatometry of a sample that transformed to martensite, following the methodology presented in Ref. [34]. The calculated values for the density of martensite and austenite used in this study are

\[
\rho_{\text{austenite}} = 7.764 \times 10^{-12} \pm 0.002 \times 10^{-12} \text{ g/\mu m}^3 \quad \text{and} \quad \rho_{\text{martensite}} = 7.782 \times 10^{-12} \pm 0.005 \times 10^{-12} \text{ g/\mu m}^3.
\]
During the derivation of \( dL/dT \) in Equation (5) it is assumed that \( \frac{L_0}{a_0} \) is very close to unity. This only holds for a material with \( \pi(T - T_0) \ll 1 \), where \( \pi \) is the average linear thermal expansion coefficient between \( T_0 \) and \( T \). This condition holds for most typical materials. For the case of austenite to bainite transformation in an 8.8 mm long sample the elongation is approximately 30 µm, considering this factor as unity involves an error of approximately 3 \( \times 10^{-3} \).

In calculating \( C_i \), it was assumed that \( \lambda_i - \lambda_1 \) is constant. This is a reasonable assumption for typical materials. The temperature dependence of the density of an isotropic constituent at constant pressure can be expressed as \( \rho_i = \frac{\rho_{i0}}{1 + 3 \pi_i (T - T_0)} \) [36], where \( \rho_{i0} \) is the density of constituent \( i \) at temperature \( T_0 \). \( \lambda_i - \lambda_1 \) can then be expressed as:

\[
\lambda_i - \lambda_1 = \lambda_{i0} \left[ 1 + 3 \pi_i (T - T_0) \right] - \lambda_{i1} \left[ 1 + 3 \pi_1 (T - T_0) \right]
\]

where \( \lambda_{i0} \approx \rho_{i0} / \rho_0 \) is the ratio between the overall density of the sample and the density of constituent \( i \), both at room temperature. To further simplify Equation (11) it is convenient to define \( \epsilon_{i1} \equiv \frac{\lambda_{i1}}{\lambda_{i0}} - 1 \) and \( \epsilon_{i0} \equiv \frac{\lambda_{i0}}{\lambda_{i1}} - 1 \). Equation (11) can then be rearranged as:

\[
\lambda_i - \lambda_1 = \epsilon_{i1} \lambda_{i1} + 3 \epsilon_{i0} \lambda_{i0} \pi_1 (T - T_0)
\]

The assumption that \( C_i \) is constant will only hold if the first term in Equation (12) is much greater than the second term:

\[
|\epsilon_{i1} \lambda_{i1}| \gg 3 |\epsilon_{i0} \lambda_{i0} \pi_1 (T - T_0)|
\]

After rearranging and simplifying Equation (13) and keeping in mind that \( 1 - 3 \pi_1 (T - T_0) \) is close to unity and can be approximated as 1, we will get:

\[
\lambda_i - \lambda_1 \approx \epsilon_{i1} \lambda_{i1} + \epsilon_{i0} \lambda_{i0} \pi_1 (T - T_0)
\]

Equation (14) can be simplified to:

\[
3|\pi_1 (T - T_0)| \ll \frac{\rho_{i0}}{\rho_0} - 1
\]

Equation (15) shows that \( C_i \) is approximately constant when the effect of difference in density between constituents is much greater than the effect of differential linear thermal expansion coefficients. For the case of austenite decomposition to bainite the right hand side of Equation (15) is \( 1.4 \times 10^5 \) times greater than the left hand; therefore, assuming a constant \( C_i \) is reasonable.

In calculating \( C_i \), it was mentioned that a linear fitting to the derivative of the dilation curve is sufficient for capturing the variations with temperature. In other words, \( \lambda_{i0} \) is approximately proportional to the change in temperature. Using the temperature dependence of density introduced in the previous paragraphs, \( \lambda_{i0} \) can be rewritten as:

\[
\lambda_{i0} = \lambda_{i0} \left[ 1 + 3 \pi_i (T - T_0) \right] c_i
\]

If \( 3 \pi_1 (T - T_0) \ll 1 \), then \( \lambda_{i0} \) will be proportional to \( a_0 \). For most materials \( a_i \) changes approximately linearly with temperature and \( \lambda_{i0} \) can be tracked using a linear fitting to the derivative of the dilation curve. In the case of austenite decomposition to bainite \( 3 \pi_1 (T - T_0) \approx 3 \times 10^{-3} \) which is much less than unity and therefore, using a linear fitting to capture the changes with temperature is reasonable.


