Modelling Simultaneous Formation of Bainitic Ferrite and Carbide in TRIP Steels

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The addition of 1.5–2 wt% Si is a commonly used alloying approach for TRIP steels. Si delays cementite precipitation during bainite transformation thereby enabling that an adequate amount of austenite can be retained at room temperature due to sufficient carbon enrichment. However, the degree of cementite prevention and thus the fraction of retained austenite depend on the employed processing parameters and steel chemistry. The present work proposes a modelling framework to quantify the delayed carbide precipitation during bainite formation. A nucleation-growth based model describes the simultaneous formation of bainitic ferrite and cementite precipitation for various continuous cooling scenarios. The retarding effect of Si on cementite precipitation is explicitly accounted for. The fraction of bainite and the carbon content of the remaining austenite, which determines the Ms temperature of remaining austenite, can be tracked along non-isothermal processing paths. The proposed model is evaluated using continuous cooling transformation data for a 0.19C–1.5Mn–1.6Si–0.2Mo (wt%) steel.

KEY WORDS: carbide-free bainite; bainite growth; cementite precipitation; martensite start.

1. Introduction

Transformation Induced Plasticity (TRIP) steels contain retained austenite in the final microstructure and this leads to an attractive property combination of high strength with large uniform and total elongation. The morphology, fraction and stability of retained austenite are determined during the bainite transformation stage, where due to Si and/or Al addition carbide precipitation is retarded. Thus the remaining austenite is expected to be further enriched with carbon as bainitic ferrite forms. Although this transformation product is frequently referred to as carbide-free bainite, strictly speaking, it is not consistent with the classical definition of bainite. Furthermore, in contrast to the common perception, the formation of carbide-free bainite in Si-containing TRIP steels is not necessarily a true assumption. There are a number of observations confirming some carbide precipitation depending on steel composition and processing conditions. For example, a thorough transmission electron microscopy (TEM) study of bainite microstructures in high carbon Si–Mn TRIP steels indicated that cementite precipitates in conjunction with bainitic ferrite for most of the investigated transformation temperatures, i.e. 300–450°C, despite short reaction times and high Si content of 1.5 wt%. In addition, indirect evidence based on the measurement of martensite start temperature, Ms, implies that carbide must have precipitated during continuous cooling formation of bainite in a steel with a Mo-TRIP chemistry (0.2 wt%C–1.5 wt%Mn–1.6 wt%Si–0.2 wt%Mo). These observations, together with additional examples in the literature, suggest that carbide has to be considered as a potential constituent of bainite in TRIP steels. The degree of carbide precipitation will determine the amount of carbon enrichment of austenite which is the most important factor for the stability of austenite and thus critically determines the amount of austenite that can be retained at room temperature.

The final microstructure including the fraction of retained austenite of TRIP steels is very sensitive to the employed processing path. Therefore, developing a predictive microstructure model is paramount to predict the overall kinetics of bainite formation and to track the variation of carbon content of remaining austenite along the processing path. Currently available models for bainite formation mainly consider either the formation of carbide-free bainite or deal with the combined kinetics of bainitic ferrite and carbide as an aggregate. Further, the influence of Si on delaying cementite precipitation was not accounted for in attempts dealing with simultaneous formation of carbide and bainitic ferrite. Accurate prediction of bainite formation kinetics and proper estimation of the retained austenite volume fraction require the explicit inclusion of the retarding effect of Si on carbide precipitation. A first generation bainite model had previously been developed for a Mo-TRIP steel where the overall kinetics of bainitic ferrite formation and carbide precipitation were modeled using a semi-empirical approach. Two parameters were introduced to describe the amount of retained austenite as a function of the bainite formation temperature: (i) the degree of carbide precipitation and (ii) the carbon diffusion distance in remaining austenite. The empirical parameters of the carbide precipitation model were obtained based on the estimation of the carbide fraction precipitated as inferred from the martensite start temper-
temperatures, $M_s$, observed in continuous cooling transformation tests.

In the present work a nucleation-growth based modelling framework is proposed that captures the simultaneous formation of bainitic ferrite and cementite in a more rigorous fashion for TRIP steel chemistries. It is out of the scope of the current work to analyze and discuss shear\(^{11}\) and diffusional approaches\(^{12}\) of bainite. Over the past decades many aspects of the bainite reaction were described successfully in terms of a diffusional mechanism that is therefore adopted here. The proposed model is aimed at predicting the fraction of bainite and carbon content of the remaining austenite along complex processing routes. The model is applied to the previously studied Mo-TRIP steel for which a set of experimental transformation data is available.

2. Experimental Data

The examined material is a laboratory cast steel containing 0.19C–1.5Mn–1.6Si–0.2Mo (wt%) and supplied as hot-forged bars by ArcelorMittal Dofasco (Hamilton, ON). This material was previously subjected to a thorough investigation and the kinetics of austenite decomposition were characterized for a wide range of thermo-mechanical processing conditions.\(^{3}\) For a detailed description of the experimental procedures, as well as the complete set of measurements readers are referred to our previous article.\(^{4}\) In the present work selected continuous cooling conditions are analyzed in depth where bainite transformation is preceded by ferrite formation. Table 1 depicts these scenarios in terms of reheating temperature, resulting austenite grain size, $d_o$, and subsequent cooling rate, CR. Further, Table 1 provides the relevant experimental data for the fraction of prior ferrite, $f_o$, the carbon content, $C_{\text{attrans}}$, and the grain diameter, $d_{\text{attrans}}$, of the untransformed austenite, the bainite transformation start temperature, $B_s$, bainite fraction transformed, $f_b$, and martensite start temperature, $M_s$. Untransformed austenite denotes the austenite that is present at $B_s$ and its carbon concentration and grain size are estimated as $c_o/(1-f_o)$ and $d_o(1-f_o)$, respectively. Here, $c_o$ is the nominal carbon concentration of the steel. Figure 1 gives a typical example of the transformation kinetics and its derivative ($df/dT$) for the investigated steel. The austenite decomposition appears to be sequential with a transformation curve consisting of three sub-segments, the onset of individual transformation, i.e. $B_s$ and $M_s$, can be readily determined from the measured kinetic data, as illustrated in Fig. 1. The local minima in the transformation rate can, as labeled, be taken as indication for the bainite and martensite start temperatures. For all these cooling conditions, no retained austenite was observed indicating that the C enrichment of austenite was insufficient which, at least in part, can be attributed to cementite precipitation.

Figure 2 shows an example of the resulting microstructures, i.e. here for $d_o=34$ μm and CR=1°C/s, which primarily consists of ferrite and bainite. It was found that for most of the cases where $f_o>0.08$ (cf. Table 1) the prior austenite grain boundaries are entirely covered by ferrite grains such that upon further cooling bainite can nucleate only at ferrite/austenite inter-phase boundaries.

3. Model Development

The overall model for bainite formation applicable to TRIP steels needs to address two main features: (i) the onset temperature of the bainite reaction following ferrite formation, and (ii) the kinetics of bainite growth. The latter includes two sub-models that deal with simultaneous formation of bainitic ferrite and cementite precipitates from the remaining austenite. The predicted $M_s$ temperature of the remaining austenite and thus the fraction of the retained austenite rely on the outcome of these two sub-models. The

Table 1. Selected processing conditions and relevant experimental data.

<table>
<thead>
<tr>
<th>$T_{\text{Reheating}}$</th>
<th>$d_o$, μm</th>
<th>CR, °C/s</th>
<th>$f_o$</th>
<th>$C_{\text{attrans}}$, wt%</th>
<th>$d_{\text{attrans}}$, μm</th>
<th>$B_s$, °C</th>
<th>$f_b$</th>
<th>$M_s$, °C</th>
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<td>24</td>
<td>1</td>
<td>0.55</td>
<td>0.42</td>
<td>18</td>
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<td>0.33</td>
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<td>10</td>
<td>0.05</td>
<td>0.20</td>
<td>24</td>
<td>620</td>
<td>0.62</td>
<td>380</td>
</tr>
<tr>
<td>1050°C</td>
<td>34</td>
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<td>0.43</td>
<td>0.33</td>
<td>28</td>
<td>590</td>
<td>0.41</td>
<td>300</td>
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<tr>
<td></td>
<td>34</td>
<td>5</td>
<td>0.08</td>
<td>0.21</td>
<td>33</td>
<td>618</td>
<td>0.66</td>
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<td>0.03</td>
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<td>620</td>
<td>0.51</td>
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<td>620</td>
<td>0.62</td>
<td>390</td>
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Fig. 1. (a) Examples of the measured overall transformation kinetics indicating that the decomposition of austenite into ferrite and bainite is sequential for the examined conditions, (b) the variation of the transformation rate with temperature showing separate peaks associated with each transformation product.

Fig. 2. Example of microstructure resulting from continuous cooling transformation ($T_{\text{Reheating}}=1050°C$, $d_o=34$ μm, CR=1°C/s).
model assumes that during the austenite-to-bainite transformation only carbon can redistribute, i.e. the substitutional sub-lattice remains frozen. Then the paraequilibrium condition provides the reference for evaluating the required thermodynamic parameters.

3.1. Onset of Bainite Formation
A phenomenological approach is adopted to describe the Bₙ temperature of the untransformed austenite. The bainite reaction starts once a critical driving pressure \( G_{\text{critical}} \) is attained. For the present steel, a linear temperature dependence is obtained for this critical driving pressure, i.e.\(^4\)

\[
G_{\text{critical}} (J/m^4) = 3.64 T(°C) - 2840 \quad (1)
\]

The above equation represents the critical value of the driving pressure \( \Delta G_{\text{N}}^{\text{cu}} \) for the nucleation of bainitic ferrite from austenite with an average carbon content \( c_f = c_f^{\text{at}} \) at the experimental bainite start temperatures. The value of \( \Delta G_{\text{N}}^{\text{cu}} \) is a function of temperature and the carbon content of austenite.

The concept of a critical driving pressure had been originally proposed by Ali and Bhadeshia.\(^13\) However, they favour a displacive transformation mechanism for bainite formation even though the proposed nucleation criteria are based on the partitioning of carbon atoms. Thus, Eq. (1) constitutes a criterion for diffusional formation of bainitic ferrite in the present work.

3.2. Bainitic Ferrite Formation
The overall kinetics of bainitic ferrite formation is described as concurrent nucleation and growth processes in the framework of the diffusional mechanism. For simplicity, bainitic ferrite laths are assumed to have a circular cross section nucleating at austenite-ferrite boundaries. The growing tip of the laths has a curvature of \( \rho \). The lath thickness, which corresponds to its diameter, is temperature and composition dependent. The classical nucleation theory is used to assess the temporal evolution of the bainitic ferrite lath number density \( N_B \). The time that a critical nucleus needs to turn into a lath is assumed to be negligible. The nucleation rate is given by

\[
\frac{dN_B}{dt} = N_B' (1 - F_B - F_\theta) \exp \left( \frac{Q_{a-r}}{kT} \right) \exp \left( - \frac{\lambda}{(\Delta G_{\text{N}}^{\text{cu}})^2 kT} \right) \quad (2)
\]

where \( F_B \) and \( F_\theta \) denote fraction of bainitic ferrite and cementite, respectively, normalized by \((1-f_a)\), i.e. the fraction of untransformed austenite at bainite start. \( Q_{a-r} \) is the activation energy for an iron atom crossing the interface from parent matrix to the growing sub-critical cluster, \( \lambda \) is self diffusion in ferrite, \( \sigma_{\text{RT}} \) and geometrical factors, \( h \) is Planck’s constant and \( kT \) has its usual meaning. The initial number of potential nucleation sites, \( N_B^{\text{at}} \), is proportional to the surface area of austenite-ferrite boundaries that is related to the initial austenite grain size and fraction of polygonal ferrite by

\[
N_B^{\text{at}} = \frac{\eta}{d_s(1-f_a)^{1/3}} \quad (3)
\]

where \( \eta \) is a constant. The nucleation equation provides the number of bainitic ferrite laths formed in each time step. The diameter of a cylindrical lath, i.e. its thickness, is calculated using an empirical equation fitted to experimental data from the literature\(^4\) as a function of temperature and the average carbon content of parent austenite, i.e.

\[
w_B(\mu m) = \left[ 4.2 \times 10^{-4} T(°C) - 8.7 \times 10^{-2} \right] \frac{c_f^{\text{at}}}{c_f^{\text{at}}(\text{wt} \%) } \quad (4)
\]

The lengthening rate of laths is described in terms of a carbon diffusion-controlled, edge-wise growth mechanism such that the growth rate of a bainitic ferrite lath can be calculated using the Zener-Hillert formulation\(^15\)

\[
v_B = \frac{1}{2 \rho} (c_f^{\text{at}} - c_f) D_c^{\text{eq}} \quad (5)
\]

where \( D_c^{\text{eq}} \) is the carbon diffusivity in austenite and \( c_f^{\text{at}} \) is the equilibrium carbon concentration along the tip of the bainitic ferrite-austenite interface, corrected to account for the capillary effect. In addition to the capillary effect other factors may affect the interface composition, e.g. solute drag, interface reaction and selection of alternative local equilibrium conditions at the interface, and influence the supersaturation term, \( c_f^{\text{at}} - c_f \) in Eq. (5). For simplicity, paraequilibrium treatment is used for the assessment of supersaturation based on the \( A_{\text{at}} \) boundary without correction for the presence of additional growth barriers.\(^16,17\) Then bainite growth ceases once the average carbon of remaining austenite attains the paraequilibrium \( A_{\text{at}} \) line.

In the Zener-Hillert formulation, as \( \rho \) changes, and so does \( c_f^{\text{at}} \), the lengthening rate changes accordingly. It is assumed that the system adopts a tip curvature corresponding to the maximum growth rate \( V_{\text{max}} \). The maximum growth rate of bainite laths was determined as a function of austenite carbon content and reaction temperature for the investigated material as described in the Appendix. Figure 3 shows the variation of \( V_{\text{max}} \) with carbon content and temperature. In the present case, the maximum growth rate peaks around 525°C regardless of the carbon content of austenite.
Further, the growth of bainitic ferrite decreases with increasing carbon enrichment of the remaining austenite, i.e. the maximum growth rate at 525°C drops from 200 μm/s to 20 μm/s as the carbon content increases from 0.19 to 1 wt%.

The overall rate of bainitic ferrite formation is then calculated using the following rate equation

$$\dot{f}_B = \frac{dF_B}{dt} = \frac{\pi r^2_B}{4} N_{gh} V_{max} (1 - F_B - F_\theta) \quad \text{(6)}$$

employing two adjustable parameters, i.e. $\lambda$ and $\eta$. At any instance, the real fraction of bainite, $f_B$, in the final microstructure can be calculated using an appropriate multiplication factor, i.e. $f_B = \Psi F_B$. This factor is defined by

$$\Psi = \frac{c_{PE}^\gamma - c_a}{c_{PE}^\gamma - c_{PE}^{\gamma}} \quad \text{(7)}$$

where, $c_{PE}^\gamma$ and $c_{PE}^{\gamma}$ are the paraequilibrium carbon content of ferrite and austenite, respectively.

### 3.3. Nucleation and Growth of Cementite

The formation of bainitic ferrite gives rise to carbon enrichment of the remaining austenite. The thermodynamic condition for the precipitation of cementite is fulfilled once the austenite is super saturated with respect to the carbon solubility, $c_{Acm}$ given by the $Acm$ line, i.e. the austenite/austenite + cementite (γ+γ′) phase boundary. The nucleation of cementite particles from austenite on heterogeneous nucleation sites is described by the classical nucleation formulation

$$N_\theta = \frac{dN_{gh}}{dt} = N_\theta' (1 - F_B - F_\theta) \frac{KT}{h} \exp\left\{ \frac{Q}{RT} \exp\left\{ - \frac{\kappa \sigma}{(\Delta G^{N=0})^3} \right\} kT \right\} \quad \text{(8)}$$

where $N_\theta'$ is the potential number of nucleation sites, $Q$ denotes the activation energy for carbon diffusion in austenite, $\Delta G^{N=0}$ is the nucleation driving pressure of cementite from austenite, which is proportional to the undercooling below the $Acm$ phase boundary. The parameter $\kappa$ is a constant related to the potency of heterogeneous nucleation sites and $\sigma$ is the interfacial energy.

The radial growth rate of cementite particles (with radius $r_\theta$) is estimated by means of the Zener equation,\(^{18}\) together with an extra term that accounts for the effect of new arriving nuclei (with radius $r^*$), i.e.

$$r_\theta = \frac{dr_\theta}{dt} = \frac{D_c^*}{r_\theta} \left( c_c^\gamma - c_{Acm} \right) + \frac{dN_\theta}{dt} \left( \frac{r^* - r_\theta}{N_\theta} \right) \quad \text{(9)}$$

where $c_c^\gamma$ is the carbon content of cementite and $r^*$ is the size of the critical nucleus, i.e.

$$r^* = \frac{\sigma}{2 \Delta G^{N=0}} \quad \text{(10)}$$

The volume fraction of cementite in the remaining austenite is given by

$$F_\theta = \frac{4}{3} \pi r^3 \frac{N_\theta}{N_\theta'} \quad \text{(11)}$$

assuming spherical cementite particles. The real fraction of cementite in the overall microstructure is given by: $F_\theta (1 - f_\theta)$. In the present analysis, $N_\theta'$, $\kappa$ and $\sigma$ are serve as adjustable parameters.

The proposed cementite precipitation in austenite is consistent with the formation of upper bainite but can be applied to lower bainite as well. Even though the classical view suggests that carbides in lower bainite are intralath particles within ferrite, there is significant evidence that carbide precipitation occurs also in this case from austenite. Spanos et al.\(^{19}\) have shown through TEM studies that lower bainite involves initially the formation of a carbide free ferrite spine followed by sympathetic nucleation of several sidewise ferrite platelets at 60° inclination angle. The carbide particles precipitate from enriched austenite between the secondary ferrite platelets. A subsequent coalescence stage brings about a monolithic lower bainite sheave that appears as if carbide would have precipitated within the ferrite laths.

### 3.4. Carbon Mass Balance

The evolution of carbon concentration in the remaining austenite is controlled by two counterbalancing factors, i.e. bainitic ferrite formation and cementite precipitation, such that

$$\dot{c}_\gamma = \frac{dc_\gamma}{dt} = \frac{1}{1 - F_B - F_\theta} \left[ \frac{dF_B}{dt} (c_c^\gamma - c_B) - \frac{dF_\theta}{dt} (c_\theta - c_\gamma) \right] \quad \text{(12)}$$

Further, at each time step the conservation of carbon mass is verified via a carbon mass balance equation, i.e. $c_\gamma = \sum f_i c_i$ has to be zero.

The $M_s$ temperature of the remaining austenite is calculated using $c_\gamma$ and well-known empirical equations, e.g. for $c_\gamma < 0.8$ wt%\(^{20}\)

$$M_s(°C) = 561 - 474 \text{ wt%C} - 33 \text{ wt%Mn} - 21 \text{ wt%Mo} \quad \text{(13)}$$

and for $c_\gamma > 0.8$ wt%\(^{21}\)

$$M_s(°C) = 420 - 208.33 \text{ wt%C} - 33.4 \text{ wt%Mn} + 1.29 \text{ wt%Mo}^2 - 24.3 \text{ wt%Mo} \quad \text{(14)}$$

### 3.5. Calculation of Paraequilibrium Phase Boundaries

The relevant phase boundaries and driving pressures for the nucleation of various phases from austenite have been calculated with respect to paraequilibrium condition. As substitutional species are not allowed to partition in paraequilibrium treatment, the site fraction occupied by individual elements in the substitutional sublattice remains unchanged during austenite decomposition. This constraint can be readily applied for growing bainitic ferrite, however the presence of Si constitutes additional complexity for the calculation of the cementite/austenite phase boundary under paraequilibrium. The Si atoms are insoluble in cementite. Nevertheless, there is evidence indicating that the substitutional alloy content of cementite that forms during tempering is the same as that in the parent phase.\(^{22,23}\) The experimental thermo-chemistry data on Si-containing cementite is scarce and it is not included in the current Fe database of the Thermo-Calc software. In order to assess the free energy of metastable cementite with a given site fraction of Si in
the substitutional sublattice a suitable value for the heat of Si\(_2\)C formation from C and Si is required. Gosh and Cohen proposed 250 kJ/mol based on a trial and error approach of analyzing the Fe–C–Si and Co–C–Si systems.\(^{22}\) Cementite proposed 250 kJ/mol based on a trial and error approach of the binary Si–C system. The formation energy of \(\text{Si}_3\text{C}\) compound for Si\(_2\)C by Gosh and Cohen had been chosen to fulfill these requirements. This proposed energy of formation is very similar to that calculated for Si\(_2\)C by means of first principles density functional theory (DFT) simulations, \(i.e.\ 256.4\ \text{kJ/mol}.\(^{23}\)

The calculated paraequilibrium phase boundaries are depicted in Fig. 4 for the examined steel. For the assessment it was assumed that the site fraction of Mn, Si and Mo in the substitutional sublattice of various phases, \(i.e.\) ferrite, austenite and cementite, is identical. The required data for construction of Gibbs energy curves under paraequilibrium were retrieved from Thermo-Calc version N with Fe2000 database using TQ interface and a FORTRAN code. To permit dissolution of Si in cementite, the Fe2000 database was modified to include thermo-chemistry data of Si\(_3\)C in the binary Si–C system. The formation energy of Si\(_3\)C compound from graphite carbon and diamond Si was introduced as the only parameter without temperature dependence. The \(A_{\text{cm}}\) boundary is very sensitive to the value assumed for the formation energy of Si\(_3\)C; 250 kJ/mol displaces \(A_{\text{cm}}\) toward lower temperatures whereas negligible formation energy, \(i.e.\) approaching 0 J/mol, raises \(A_{\text{cm}}\) by about 200°C. A hypothetical constraint condition in which carbon and Si atoms partition completely while Mn and Mo remain immobile in the substitutional sublattice is also illustrated for the sake of comparison by the dashed line in Fig. 4. The lowest \(A_{\text{cm}}\) boundary associated with 250 kJ/mol requires an unrealistic high supersaturation for carbon in austenite to permit the precipitation of cementite. This level of carbon supersaturation is very unlikely in practice; even for interlath austenite, and the thermodynamic condition for precipitation of cementite can never be fulfilled. In the present study a negligible, positive formation energy for Si\(_3\)C is assumed that permits cementite to form under sufficient carbon supersaturation of austenite consistent with experimental observations.

### 3.6. Numerical Scheme and Optimization of Model Parameters

The decomposition of the untransformed austenite into bainite below the B\(_{\text{s}}\) temperature is evaluated by numerical integration of the above five differential rate equations, \(i.e.\ \dot{N}_\text{M}, \dot{F}_\text{B}, \dot{N}_\text{G}, \dot{F}_\text{B}\) and \(\dot{c}_\text{A}\), along a given cooling path. In each time step, \(\Delta t\), and for an instantaneous carbon content of austenite new fractions of bainitic ferrite and cementite are separately calculated using the first four equations adopting the information from the previous time step. Subsequently by means of the last equation the composition of austenite is updated and a new \(M_t\) temperature for the remaining austenite is calculated. The code executes the aforementioned iteration for each successive, infinitesimally small isothermal step until the \(M_t\) temperature is attained.

**Table 2** gives the list of physical quantities and constants used in the model. In addition, there are five adjustable parameters, \(i.e.\) \(\lambda, \eta, N_0, \kappa\) and \(\sigma_{0y}\). An appropriate combination of these parameters has to be determined such that the experimental measurements for the nine processing conditions (Table 1) can be adequately described. The experimental data are compared with the model calculations in terms of the \(M_t\) temperature of the remaining austenite, the final bainite fraction, \(f_{\text{max}}\) as well as the bainite fraction at midway between \(B_s\) and \(M_t\), temperatures, \(f_{\text{mid}}\). On this basis the sum, \(S\), of the deviations of measured and calculated values, \(i.e.\)

\[
S = \sum_i \left( \frac{M_\text{exp}^{\alpha} - M_\text{calc}^{\alpha}}{M_\text{exp}^{\alpha}} + \frac{f_\text{exp}^{\alpha} - f_\text{calc}^{\alpha}}{f_\text{exp}^{\alpha}} + \frac{f_\text{mid}^{\alpha} - f_\text{calc}^{\alpha}}{f_\text{mid}^{\alpha}} \right)
\]

\[\text{(15)}\]

has to be minimized. The Genetics Algorithm (GA) Toolkit of MATLAB was used for the optimization purpose to find the five fit parameters.

A FORTRAN code was developed to numerically integrate the rate equations and to assess the thermodynamic properties of the system in paraequilibrium condition. The required data were retrieved from Thermo-Calc version N with Fe2000 database. A supplementary MATLAB program was coded to call the executable FORTRAN code and to

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**Table 2.** List of constants and physical quantities used in the model.

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<th>Symbol</th>
<th>Value</th>
<th>Comment</th>
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</tr>
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<td>(h)</td>
<td>6.626×10^{-36} \text{ kg m}^2\text{s}^{-1}</td>
<td>From Ref. 20)</td>
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<td>(Q_{\text{Fe}2\text{C}})</td>
<td>275 \text{ kJ/mol}</td>
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<td>(V_{\text{max}})</td>
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<tr>
<td>(c_{\text{Fe}}, c_{\text{PE}}, c_{\text{Acm}}, c_{\theta})</td>
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<td>(\Delta G_{\alpha}^{\gamma}) and (\Delta G_{\gamma}^{\alpha})</td>
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<td>(\text{J m}^{-2})</td>
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**Table 3.** Adjusted values of model parameters used for the simulations.

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<th>(\eta, \text{m}^{-3})</th>
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mimic the object function, $S$, with its output to be minimized in the GA toolkit.

4. Model Prediction and Discussion

Figure 5 shows the comparison of the optimized model calculation with the experimental kinetics of bainite formation. The adjustable model parameters used for the simulations are depicted in Table 3. For the two smaller austenite grain sizes (24 and 34 μm) the model describes the experimental data with sufficient accuracy. In contrast, for the highest reheating temperature corresponding to $d_o=52$ μm, the model has a tendency to underestimate the experimental transformation rate and the discrepancy tends to become more pronounced as cooling rate increases. This apparent discrepancy may be related to the increasing role of autocatalytic nucleation for larger austenite grain sizes. The formulation of bainite nucleation in the model does not explicitly account for different nucleation modes.

The other important simulation result is related to the kinetics of cementite precipitation and the resulting carbon content of austenite that determines the martensite start temperature, $M_s$, which also provides the criterion for the stop of the bainite formation and the resulting final bainite fraction. Thermodynamically cementite precipitation is possible only below the $A_{cm}$ boundary, and thus remaining austenite must be sufficiently enriched with C during either ferrite or bainitic ferrite formation. Figure 6 shows representative examples of the evolution of the carbon content of austenite, $c_\gamma$, with temperature during bainite formation for various cooling rates. This figure shows also the $A_{cm}$ boundary as well as $M_s$ as a function of carbon content. The starting point for each curve indicates the carbon enrichment of the remaining austenite at the $B_s$ temperature. In the present cases, the prior ferrite reaction is rather limited such that the resulting carbon enrichment of austenite is modest. The carbon content of austenite falls in the range of 0.2–0.35 wt% well above the $A_{cm}$ line at the start of bainite formation. As a result, initially bainite forms without simultaneous cementite precipitation and the remaining austenite is further enriched with carbon. For the largest cooling rate of 10°C/s the amount of bainite formation is limited such that the $M_s$ temperature is reached before carbon enrichment beyond the $A_{cm}$ line can be attained. For the lower cooling

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**Fig. 5.** Comparison of experimental and calculated kinetics for continuous cooling bainite formation from different austenite grain sizes.
rates of 1 and 5°C/s the scenario is different. Here, with the aid of carbide-free bainite formation additional enrichment beyond the \( A_{\text{cm}} \) boundary becomes possible. At this stage, although cementite can thermodynamically precipitate, due to kinetic constraints the precipitation is further delayed to an undercooling of approximately 20°C below the \( A_{\text{cm}} \) boundary. Subsequent cooling leads to significant formation of cementite and associated carbon depletion of the remaining austenite. The calculated maximum carbon content in austenite provides the condition at which carbon depletion due to cementite precipitation dominates carbon enrichment as result of bainitic ferrite formation. In the present simulations, the carbon level of remaining austenite drops quickly to reach the \( M_s \) temperature. Matching the experimental \( M_s \) temperatures provides guidance to select nucleation parameters for cementite precipitation in austenite. It is worthwhile to note that with the absence of carbide precipitation a much lower \( M_s \) temperature would be predicted for the 1 and 5°C/s cases.

The carbon evolution in remaining austenite, as shown in Fig. 6, is determined by a competing interplay between bainitic ferrite formation and carbide precipitation that may lead to either carbon enrichment or depletion. The relative contribution of each event varies as temperature changes and the net effect controls the dependence of carbon content of remaining austenite with temperature. For the examined continuous cooling scenarios the measured \( M_s \) temperatures (cf. Table 1) are well above room temperature implying that there is very little if any retained austenite present in the final microstructure. During industrial processing TRIP steels are usually subjected to nearly isothermal heat treatments (e.g. very slow cooling of a coil at approximately 30°C/hour) for bainite formation such that a finite fraction of austenite can be retained at room temperature. For these conditions the temperature dependency of carbon content of retained austenite, determined at the final stages of the bainite reaction, is mainly controlled by the growth rate of ferrite laths and cementite particles that scales with the \((c'_p-c_c)D_f^2\) and \((c_c-c_{A_{cm}})D_f^2\) terms (Eqs. (5) and (9)), respectively. As both terms share the carbon diffusivity, the effect of temperature stems from the supersaturation, i.e. the slope of \(\alpha+\gamma\)

\[ \text{Fig. 6. Evolution of the carbon content of the remaining austenite during continuous cooling bainite formation at 1, 5, 10°C/s. (}\Delta c=34 \mu m) \text{ Bainite reaction stops once the carbon content of the remaining austenite reaches the martensite start condition given by the dashed line. } A_{\text{cm}} \text{ line was calculated based on a negligible formation energy for SiC.} \]

and \( A_{\text{cm}} \) boundaries, which at 400°C is 0.008 wt%C/°C and 0.003 wt%C/°C, respectively. This suggests that at lower temperatures cementite precipitation slows down relatively to ferrite lath lengthening and thus its relative contribution to carbon evolution of remaining austenite tends to be less significant. The complex nature of carbon enrichment and depletion of remaining austenite can be illustrated further by analysis of data reported in the literature. For example, the carbon content of retained austenite in two similar TRIP steels but with different Si levels, i.e. 1 and 1.5 wt%, has been measured for a range of isothermal holding temperatures. The result indicates that for higher Si steel the carbon of retained austenite is almost invariable around 1.4 wt%C and does not change with reaction temperature between 360 and 440°C. In contrast for the 1.0 wt%Si steel the carbon of retained austenite is much lower and it increases rapidly from 0.7 wt%C at 460°C to approach finally to that for the higher Si steel at 360°C, i.e. 1.4 wt%C. The observation implies that at higher reaction temperatures significant cementite precipitation must have occurred for the low Si steel. One can draw the conclusion that the relative contribution of carbon enrichment and depletion in austenite is very complex and depends on several factors, e.g. Si content, reaction temperature and prior thermal history. Further, the distribution of carbon in austenite is not uniform which adds more complexity. This aspect will be discussed in the following.

Figure 7 provides a summary of the calculated \( M_s \) temperatures and final bainite fractions and their comparison with the measured values. The final bainite fractions are reasonable well captured except for the case with the largest austenite grain size (52 μm) and largest cooling rate (10°C/s), i.e. the final bainite fractions for slower cooling from the larger austenite grain size is still reasonably well described even though there are significant deviations with the experimental transformation rates (see Fig. 5). The situation for describing the \( M_s \) temperatures is different. Here, the model reasonably captures the experimental data for the lowest cooling rate (1°C/s) and for two out of three cases of the highest cooling rate (10°C/s). However, for the intermediate cooling at 5°C/s and one case at 10°C/s the measured \( M_s \) temperatures are 50–100°C higher than calculated. This may be in part related to one of the model premises of a homogeneous carbon content in the remaining austenite. This appears to be a valid assumption for slow cooling rates since there is sufficient time for redistribution of carbon atoms to reach a uniform carbon level in austenite. Then carbide precipitation and the start temperature of martensite formation
are the same in all locations of remaining austenite. The average value for carbon content, which is determined as a function of bainite fraction and the extent of cementite precipitation, captures the Ms temperature of austenite for cooling at 1°C/s.

For cooling at higher rates the rejected carbon atoms may not completely redistribute, in particular at the lower temperatures of bainite formation. Thus, a carbon concentration gradient in the remaining austenite can be expected. This will lead to locally different cementite precipitation. Far field austenite, where local carbon enrichment may be minimal, i.e. close to the initial value at the onset of bainite formation, transforms to martensite at higher temperature whereas the enriched austenite adjacent to advancing ferrite boundaries undergoes a delayed martensite formation at lower temperatures. The mean field approach of the present model is not suitable to describe this situation. Nevertheless, an apparent agreement of calculated and measured Ms has been attained in selected cases for the highest investigated cooling rate of 10°C/s. Here, the combined fraction of ferrite and bainite is sufficiently low such that the carbon enrichment of the remaining austenite is less significant for the determination of the global Ms temperature. For example, for the case shown in Fig. 7, the carbon content of austenite is calculated to increase from 0.2 to 0.37 wt% during bainite formation. This carbon enrichment lowers Ms by 80°C according to Eq. (13) and the calculated Ms value is approximately 30°C below the measured one.

5. Conclusion

A physically-based model in the framework of the diffusional approach is proposed to describe the simultaneous formation of cementite and bainitic ferrite from a dual-phase austenite-ferrite microstructure. The model is formulated to describe the bainite transformation in TRIP steels where despite a high Si content carbides can potentially precipitate depending on processing conditions and the composition of remaining austenite. Nucleation and growth equations for cementite and bainitic ferrite are coupled and the carbon content of austenite is determined from the balance of carbon enrichment due to bainite formation and carbon depletion due to cementite precipitation. This approach has been demonstrated to accurately calculate the bainite formation kinetics and martensite start temperatures for a number of cooling conditions in a 0.2 wt%C–1.5 wt%Mn–1.6 wt%Si–0.2 wt%Mo steel with austenite grain sizes below 40 μm and slow cooling rates (< 5°C/s) that are typically of interest when manufacturing TRIP steel sheets.

A limitation of the model is that a uniform carbon content of the remaining austenite is assumed. The evaluation of the stability of austenite requires more sophisticated approaches that should take into account potential gradients in the carbon levels and other aspects of the austenite phase, e.g. its morphology and size.

Nevertheless, the proposed framework can potentially be implemented into microstructure evolution models for TRIP and other classes of high strength steels. For example, in dual-phase steels one can determine the critical cooling rate above which bainite can be prevented upon cooling from the intercritical region. Based on the complexity of the bainite reaction, these model advancements will require appropriate experimental measurements.

Acknowledgements

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REFERENCES


Appendix

Calculation of maximum velocity for edgewise growth

According to the Zener-Hillert formulation, i.e. Eq. (5),

\[ v_B = \frac{1}{2 \rho} \left( \frac{C_p - C_m}{C_p} \right) D_C \]

the growth rate, \(v_B\), of a plate is inversely related to the radius of curvature, \(\rho\). Further, the interfacial carbon concentration, \(C_p\), of a growing ferrite plate in equilibrium with surrounding austenite, depends on the tip curvature due to capillary effect that scales with \(2\sigma_{\text{tip}}/\rho\). Here \(\sigma_{\text{tip}}\) denotes interfacial energy between ferrite and austenite. The capillary effect increases the Gibbs free energy of ferrite and thereby the interfacial carbon concentration decreases with curvature. The variation of \(C_p\) with radius of curvature is illustrated in Fig. A1 for different temperatures. For a given value of curvature the free energy of ferrite was raised by \(2\sigma_{\text{tip}}/\rho\) and the carbon equilibrium content of austenite was determined using the common tangent construction in the paraequilibrium pseudo binary phase diagram for the Fe–
1.5%Mn–1.6%Si–0.2%Mo system. For the interfacial energy an arbitrary value of 0.2 J m⁻² was assumed. Having determined the variation of \( \gamma \) with temperature and curvature, one can calculate the growth rate of a bainitic ferrite plate using the Zener-Hillert equation. The calculated growth rate tends to be zero at a critical tip curvature, passes through a maximum and subsequently approaches zero asymptotically. This growth rate behaviour is illustrated in Fig. A2 for different reaction temperatures. In this example, the mean-field carbon concentration of parent austenite is 0.6 wt%.

It is often assumed that the lengthening rate of a ferrite plate occurs at the maximum rate; i.e. the system adopts a curvature that leads to the fastest growth and thereby the highest rate for dissipation of chemical driving pressure. Hence the maximum growth velocity was determined from the derivative of Eq. (5) for different temperatures and various carbon contents of parent austenite. It has to be noted that the formation of ferrite leads to enrichment of remaining austenite with carbon such that the dependency of maximum growth rate on carbon content has to be assessed. Further, \( V_{\text{max}} \) scales with the value selected for \( \sigma_{\alpha} \gamma \) but \( \sigma_{\alpha} \gamma \) does not change the trend for \( V_{\text{max}} \) with temperature and carbon concentration. In the present bainite model (Eq. (6)), the rate of transformation is proportional to \( V_{\text{max}} \), and the number of bainite laths, \( N_{B} \). The latter, is proportional to \( \eta \), the adjustable parameter in the nucleation model (see Eqs. (2) and (3)). Thus, the variation of the scaling factor for \( V_{\text{max}} \) due to a different interfacial energy can be combined with \( \eta \) as an effective parameter, i.e. the assumption of an arbitrary value for the interfacial energy does not affect the outcome of the proposed bainite model.

To facilitate the implementation of \( V_{\text{max}} \) into the numerical code, the following expression was fitted to the calculated values for the maximum velocity:

\[
V_{\text{max}}(c_{\gamma}, T) = \frac{A_{1}}{1 + \left( \frac{(T - A_{2})}{A_{3}} \right)^{2} \left[ 1 + \left( \frac{(c_{\gamma} + A_{4})}{A_{5}} \right)^{2} \right]}
\]

where, the parameters \( A_{1} \) to \( A_{5} \) are given by:

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<th>Parameter</th>
<th>Value</th>
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