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Avila, Daniel dos Santos; Offerman, S. Erik; Santofimia, Maria J.

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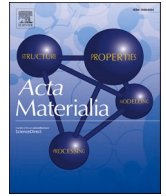
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## Modeling the effect of prior austenite grain size on bainite formation kinetics

Daniel dos Santos Avila<sup>\*</sup>, S. Erik Offerman, Maria J. Santofimia

Department of Materials Science and Engineering, Delft University of Technology, Mekelweg 2, 2628 CD, Delft, The Netherlands

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### ABSTRACT

While experiments show that refining the prior austenite grain size can either accelerate or decelerate bainite formation in steels, kinetic models based on the successive nucleation of bainitic ferrite subunits can only predict an acceleration. In this work we develop a physically-based model for bainite kinetics assuming a displacive growth mechanism which is able to reproduce both faster and slower bainite formation kinetics induced by austenite grain refinement. A theoretical analysis of the model and comparison against published experimental data show that slower kinetics for smaller grains is favored as the difference between the activation energy for grain boundary and autocatalytic nucleation of bainite increases, and as the austenite grain refinement results in finer bainite sub-units. We also theoretically analyze the density of initially present potential nucleation sites for bainite and show that the values of density used in other published bainite nucleation models are mostly underestimated. After using physically consistent values for the density of potential nucleation sites, we were able to calculate the apparent lengthening rate of bainite sheaves which were in line with experimentally measured lengthening rates.

#### List of symbols

$b$	Burgers vector
$C_1$	Proportionality constant between $T_h$ and carbon enrichment of the austenite
$C_2$	Proportionality constant between $T_0^i$ and carbon enrichment of the austenite
$C_A$	Number of bainite sub-units that can be formed by autocatalysis from the first bainite sub-unit nucleated at the prior austenite grain boundary
$d_y$	Prior austenite grain size
$dN/dt$	Nucleation rate of bainite
$dN_A/dt$	Nucleation rate of bainite by autocatalysis
$dN_{GB}/dt$	Nucleation rate of bainite at prior austenite grain boundaries
$E_{str}$	Strain energy
$f$	Fraction of bainite
$f_A$	Fraction of bainite formed by autocatalysis
$f_A^{max}$	Maximum fraction of bainite that can be formed by autocatalysis at time $t$
$f_{GB}$	Fraction of bainite formed by nucleation at austenite grain boundaries

$f_{GB}^{max}$	Maximum fraction of bainite that can be formed by nucleation at prior austenite grain boundaries
$f_y$	Fraction of austenite available for transformation
$G_N$	Universal nucleation function for bainite and Widmanstätten ferrite
$G_{SB}$	Stored energy of bainite
$h$	Planck constant
$k$	Boltzmann constant
$K_1$	Empirical constant from $G_N$
$K_2$	Empirical constant from $G_N$
$M_s$	Martensite start temperature
$n$	Number of atomic planes in the martensite or bainite embryo
$N_m$	Number of martensite plates
$N_{S,A}$	Density of potential bainite nucleation sites per bainite/austenite interface area
$N_{S,GB}$	Density of potential bainite nucleation sites per austenite grain boundary interface area
$N_{tA}$	Density of potential bainite nucleation sites for autocatalysis at time $t$
$N_{tGB}$	Density of potential bainite nucleation sites for grain boundary nucleation at time $t$

<sup>\*</sup> Corresponding author.

E-mail address: [D.dosSantosAvila@tudelft.nl](mailto:D.dosSantosAvila@tudelft.nl) (D.S. Avila).

$Q^*$	Activation energy for the dissociation of dislocations during nucleation of martensite or bainite
$Q_0^*$	Activation energy for overcoming the short-range barriers to dislocation movement
$Q_A$	Activation energy for bainite nucleation by autocatalysis at time $t$
$Q_{Ax^-}$	Activation energy for bainite nucleation by autocatalysis at the nominal carbon content of the steel
$Q_D$	Activation energy for a carbon atom to jump from a bainite embryo to the austenite matrix
$Q_{GB}$	Activation energy for bainite nucleation at austenite grain boundaries at time $t$
$Q_{GBx^-}$	Activation energy for bainite nucleation by autocatalysis at the nominal carbon content of the steel
$R$	Universal gas constant
$S_A$	Area of bainite/austenite interfaces per unit volume
$S_{GB}$	Area of prior austenite grain boundaries per unit volume
$T$	Temperature
$T_0$	Temperature at which $\Delta G^{y \rightarrow a}$ is zero
$T_0'$	Temperature at which $\Delta G^{y \rightarrow a}$ is equal to $-G_{SB}$ for the composition of austenite at time $t$
$T_{0x}^{\prime}$	$T_0'$ at the nominal carbon content of the steel
$T_h$	Temperature at which $\Delta G_m$ is equal to $G_N$ for the composition of austenite at time $t$
$T_{hx}$	$T_h$ at the nominal carbon content of the steel
$t$	Time
$u_L$	Length of the bainite sub-unit
$u_T$	Thickness of the bainite sub-unit
$u_W$	Width of the bainite sub-unit
$V_b$	Volume of the bainite sub-unit
$V_m$	Volume of the martensite plate
$v_L$	Lengthening rate of the bainite sheaf
$v^*$	Activation volume for martensite or bainite nucleation
$x^-$	Nominal carbon content of the steel
$X_b$	Carbon content trapped in bainite, either in solid solution, defects, or carbides
$Z$	Shape factor of the austenite grain
$a_m$	Exponent constant of the Koistinen-Marburger equation
$\Delta G_m$	Maximum change in Gibbs free energy for ferrite nucleation under paraequilibrium
$\Delta G^{y \rightarrow a}$	Difference in Gibbs free energy between austenite and ferrite with the same chemical composition
$\Delta Q$	Difference between $Q_{GB}$ and $Q_A$
$\delta$	Effective thickness of the austenite grain boundaries
$\lambda$	Autocatalytic factor
$\rho_A$	Number of atoms per unit area of the closed packed plane
$\sigma$	Interfacial energy
$\tau_\mu$	Athermal resistance to dislocation movement
$\Omega$	Atomic volume of Fe

## 1. Introduction

Understanding bainite formation is of great scientific and industrial interest. Bainitic steels, especially those in which cementite formation is inhibited, combine high strength with high toughness [1]. Despite having mechanical properties that are suited for several applications, such as automotive and pipelines for gas transport, their widespread use is sometimes hindered by processing difficulties such as long transformation times. Refining the prior austenite grain size has been proposed as a strategy to shorten the heat-treatments owing to faster bainite kinetics [2], but refinement of the prior austenite grain size sometimes slows down bainite formation [3]. Even though the literature has shown these opposing effects for decades, the underlying reasons behind these contradictory observations are not yet understood. It is, however, important to understand the effect of prior austenite grain size on bainite

formation kinetics in order to design adequate strategies to accelerate phase transformations based on microstructure control, as well as to increase the strength and toughness of steels through microstructure refinement.

These contradictory results were already shown in early reports reflecting the effect of the prior austenite grain size on bainite formation kinetics. Davenport et al. [4] reported that the prior austenite grain size does not have any effect on the kinetics of bainite formation. Barford et al. [5], however, found that smaller grains lead to faster bainite formation, and, within the limits of their study, the reaction rate was inversely proportional to the grain size. Umemoto et al. [6] also reported faster kinetics for smaller austenite grains, and stated that the influence of the grain size on the kinetics is generally less pronounced for bainite than it is for pearlite. Graham et al. [7] and Chráska et al. [8], on the other hand, found the opposite relationship. According to their results, grain refinement led to slower bainite formation. Chráska et al. [8] suggested that the contradictory results in literature were caused by the different measuring techniques being used by different researchers.

These apparent discrepancies were clarified in a study by Matsuzaki and Bhadeshia [9], in which two steels with different chemical compositions exhibited opposite behaviors. Their work demonstrated that the contradictions were not due to differences in experimental setup, but that different steels are affected differently by changes in the prior austenite grain size. Later works, most of them using high resolution dilatometry, confirmed that both acceleration of bainite kinetics by grain refinement [2,10–12] and by grain coarsening [3,13–17] are possible.

Several mechanisms explaining the influence of the prior austenite grain size were proposed. For the acceleration of bainite kinetics by grain refinement, Barford et al. [5] argued that it occurs because bainite nucleates at the grain boundaries. For the acceleration of bainite kinetics with increasing grain size, Graham et al. [7] argued that the softer matrix of coarse-grained steels offers less resistance to the displacement caused by bainite formation.

In a unified explanation, Matsuzaki and Bhadeshia [9] linked the bainite morphology to the effect of prior austenite grain size. The researchers assumed that bainite is formed by the successive nucleation of parallel plates that organize themselves in sheaves. A sheaf is created by the nucleation of a plate of bainitic ferrite at the austenite grain boundary, and grows by the successive nucleation of new plates of bainitic ferrite. These sheaves, which contain several individual plates of bainitic ferrite, were treated as the basic unit for understanding the transformation kinetics. They hypothesized that when the growth of the bainitic sheaves is faster than their nucleation at the prior austenite grain boundary, larger prior austenite grain sizes show faster bainite formation. Inversely, when nucleation at grain boundaries is faster than the sheaf growth, a smaller grain size leads to faster kinetics. Their hypothesis was supported by metallographic evidence and a model based on the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation.

Later works that measured the kinetics of bainite formation at different prior austenite grain sizes [10–12] explained their results using the hypothesis from Matsuzaki and Bhadeshia [9]. In these works, it is argued that the observed acceleration of bainite formation by the refinement of the austenite grain size was because the reaction was nucleation-dominated. However, there is no evidence from microstructural characterization supporting these claims. It is thus not clear if Matsuzaki and Bhadeshia's hypothesis and observations can be extended to all steels.

Another challenge is incorporating the effect of the prior austenite grain size in models for bainite formation kinetics. Models such as the JMAK-type used by Matsuzaki and Bhadeshia [9] are versatile and valuable. However, since these models use many parameters with no explicit physical meaning, there is a strong limitation to how much they can be interpreted in terms of the fundamental theories and mechanisms of bainite formation. For that, a comprehensive, physically-based model for bainite formation is needed.

Ravi et al. [18] developed a model based on the diffusionless theory of bainite formation that contains only physically-based parameters and distinguishes the activation energies for grain boundary and autocatalytic nucleation. The rate of bainite formation is assumed to be controlled by the nucleation kinetics, as commonly assumed in models that adopt the diffusionless theory [1,19,20]. Another commonly shared assumption among diffusionless-theory-based models is that the density of initially present potential nucleation sites is inversely proportional to the austenite grain size [18]. This leads to the conclusion that the rate of bainite formation is also inversely proportional to the grain size – provided that all other parameters stay the same –, thus contradicting the experimental observations discussed above. Also, Ravi et al.'s [18] model does not capture the effect of prior austenite grain size on the relative contribution of autocatalysis to the overall kinetics of bainite formation, as will be shown in Section 3.1.

In this work, we modify Ravi et al.'s [18] model in order to explicitly assume that the relative contributions of grain-boundary nucleation and autocatalysis are a function of the prior austenite grain size. With the proposed modifications, the new model is able to reproduce and explain both behaviors: the acceleration and the deceleration of bainite formation by grain refinement. The model also shows good agreement with experimental data extracted from the literature. We also re-analyze and discuss important parameters of the model such as the density of potential nucleation sites and the effect of the size of the bainite sub-unit.

## 2. Model

There are two disputing theories for the mechanism of bainite formation. Although both theories agree that bainite is a displacive transformation that involves carbon diffusion during nucleation, they disagree on the role of carbon diffusion during growth [1,21,22]. The model used in the present work adopts the theory of diffusionless growth. According to this theory, bainite plates – also called sub-units – grow without diffusion of carbon, similarly to martensite plates, until their growth is hindered by the plastic deformation of the austenitic matrix. Such plastic deformation is induced by the stresses associated with a displacive transformation. The first sub-units are assumed to nucleate at the austenite grain boundaries, and their formation is followed by successive nucleation of new sub-units at the tips of previously formed ones – a phenomenon hereafter called autocatalysis –, thus creating the characteristic sheaf morphology. The displacive character of the transformation prevents the sheaves from growing past austenite grain boundaries.

The assumption of nucleation with carbon redistribution results in a thermodynamical requirement given by [1]:

$$\Delta G_m < G_N \quad (1)$$

The requirement from Eq. (1) states that the maximum change in Gibbs free energy for ferrite nucleation under paraequilibrium,  $\Delta G_m$ , should be less than the universal nucleation function,  $G_N$ . The function  $G_N$  is an empirical function that represents the minimum driving force necessary for bainite nucleation. It is considered to be dependent only on temperature and is calculated as

$$G_N = K_1(T - 273.18) - K_2 \quad (2)$$

where  $K_1$  and  $K_2$  are empirical constants equal to  $3.637 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $2540 \text{ J mol}^{-1}$ , respectively, and  $T$  is the temperature in Kelvin [1]. The temperature in which  $\Delta G_m$  and  $G_N$  are equal for a certain composition is called  $T_h$ . In addition to the nucleation, diffusionless growth also needs to be possible for bainite formation, which gives rise to the condition expressed by Eq. (3):

$$\Delta G^{\gamma \rightarrow \alpha} < -G_{SB} \quad (3)$$

in which  $\Delta G^{\gamma \rightarrow \alpha}$  is the difference in Gibbs free energy between austenite and ferrite with same chemical composition, and  $G_{SB}$  is the stored energy

of bainite, assumed to be  $400 \text{ J mol}^{-1}$ . The temperature in which  $\Delta G^{\gamma \rightarrow \alpha}$  is equal to  $-G_{SB}$  is called  $T'_0$ . Also, the temperature in which  $\Delta G^{\gamma \rightarrow \alpha}$  is zero is called  $T_0$  [1]. According to this theory, bainite nucleation and growth can only happen in temperatures below both  $T'_0$  and  $T_h$ .

### 2.1. Overview of Ravi's model

The model developed by Ravi et al. [18] is based on the kinetics of bainite nucleation, which is split into two components: grain boundary nucleation and autocatalysis. Grain boundary nucleation is the one that takes place at the prior austenite grain boundaries ( $\gamma/\gamma$  interface). Autocatalysis, or autocatalytic nucleation, is the one that takes place at the interface between the bainitic ferrite and the austenite ( $\alpha_b/\gamma$  interface). In this manuscript, a brief overview of this model is provided for better understanding of the contributions proposed.

The overall bainite nucleation rate,  $dN/dt$ , is given by the sum of the nucleation rates of these two components, respectively  $dN_{GB}/dt$  and  $dN_A/dt$ , according to Eq. (4).

$$\frac{dN}{dt} = \frac{dN_{GB}}{dt} + \frac{dN_A}{dt} \quad (4)$$

The nucleation rate at the prior austenite grain boundaries is calculated using Eq. (5)

$$\frac{dN_{GB}}{dt} = \frac{kT}{h} N_{rGB} \exp\left(-\frac{Q_{GB}}{RT}\right) \quad (5)$$

where  $k$  is Boltzmann's constant,  $T$  is the temperature in Kelvin,  $h$  is Planck's constant,  $N_{rGB}$  is the density of potential nucleation sites for nucleation at prior austenite grain boundaries at time  $t$ ,  $Q_{GB}$  is the activation energy for nucleation at prior austenite grain boundaries, and  $R$  is the universal gas constant. The density of potential nucleation sites was derived by van Bohemen et al. [20] based on Magee's analysis of the nucleation of martensite [23], and is calculated as

$$N_{rGB} = \frac{6\delta}{d_\gamma} \frac{\alpha_m}{V_b} (T_h - T) f_\gamma \quad (6)$$

where  $\delta$  is the effective grain size thickness, taken as 1 nm,  $\alpha_m$  is the exponent from the Koistinen-Marburger equation for the given chemical composition,  $d_\gamma$  is the prior austenite grain size,  $V_b$  is the volume of the bainite sub-unit, and  $f_\gamma$  is the fraction of austenite available for transformation.

Similarly, the nucleation rate for autocatalysis is calculated applying:

$$\frac{dN_A}{dt} = \frac{kT}{h} N_{rA} \exp\left(-\frac{Q_A}{RT}\right) \quad (7)$$

where

$$N_{rA} = \frac{6\delta}{d_\gamma} \frac{\alpha_m}{V_b} (T_h - T) f_\gamma f \quad (8)$$

where  $N_{rA}$  is the density of potential nucleation sites for autocatalytic bainite formation at time  $t$ ,  $Q_A$  is the activation energy for autocatalytic nucleation of bainite, and  $f$  is the total fraction of bainite.

Immediately after its nucleation and diffusionless growth, a bainite sub-unit is supersaturated in carbon. The excess carbon can induce the precipitation of carbides and/or partition to the austenite. As the carbon content of austenite increases as a result of said partitioning, the composition-dependent limiting temperatures for bainite formation,  $T_h$  and  $T'_0$ , decrease, and are calculated as

$$T_h = T_{h\bar{x}} - C_1 f \left( \frac{\bar{X} - X_b}{1 - f} \right) \quad (9)$$

$$T'_0 = T'_{0\bar{x}} - C_2 f \left( \frac{\bar{X} - X_b}{1 - f} \right) \quad (10)$$

where  $T_{h\bar{X}}$  and  $T_{0\bar{X}}^i$  are respectively  $T_h$  and  $T_0^i$  for the nominal carbon content,  $C_1$  and  $C_2$  are proportionality constants,  $\bar{X}$  is the nominal carbon atomic fraction, and  $X_b$  is the atomic fraction of carbon that stays in the bainite, whether in solid solution or in the form of carbides.

A lower  $T_h$  implies a smaller undercooling for bainite nucleation, which results in a higher activation energy. The activation energies are then calculated as

$$Q_{GB} = Q_{GB\bar{X}} + K_{\Gamma} C_{\Gamma} f \left( \frac{\bar{X} - X_b}{1 - f} \right) \quad (11)$$

$$Q_A = Q_{A\bar{X}} + K_{\Gamma} C_{\Gamma} f \left( \frac{\bar{X} - X_b}{1 - f} \right) \quad (12)$$

where  $Q_{GB\bar{X}}$  and  $Q_{A\bar{X}}$  are the respectively initial activation energies for grain boundary and autocatalytic nucleation when the carbon content in the austenite is the nominal carbon content of the steel,  $Q_{GB}$  and  $Q_A$  are respectively the instantaneous activation energy for grain boundary and autocatalytic nucleation, considering carbon enrichment of the austenite, and  $K_{\Gamma}$  is a proportionality constant [24].

The fraction of available austenite decreases both because it decomposes during bainite formation, and because carbon enrichment will decrease  $T_0^i$ , thus hindering the activation of some potential nucleation sites. At any given time, the fraction of austenite available for transformation is the given by

$$f_{\gamma} = (1 - f) \left( \frac{T_0^i - T}{T_{0\bar{X}}^i - T} \right) \quad (13)$$

Finally, the nucleation rate is multiplied by the volume of the bainite sub-unit in order to calculate the rate of bainite formation,  $df/dt$ :

$$\frac{df}{dt} = \frac{dN}{dt} V_b \quad (14)$$

## 2.2. Proposed modification of Ravi's model

In the model developed by Ravi et al., the fraction of bainite nucleated at grain boundaries and by autocatalysis are distinguished. At any given stage of the transformation, the relative contribution of the two nucleation sites to the overall rate of bainite formation is determined solely by the difference in their activation energies. However, it is reasonable to expect that microstructural features, such as the prior austenite grain size and the size of the bainite sub-unit, would also influence the relative contribution of grain boundary nucleation and autocatalysis to the overall kinetics. Also, the austenite grain size and

the size of the bainite sub-unit should limit the total fraction of bainite that can nucleate at each site. In order to tackle both aspects, the geometrical assumption illustrated in Fig. 1 is proposed.

Fig. 1a shows that at the start of bainite formation only grain boundary nucleation sites are present. The maximum fraction of bainite that can be formed from these nucleation sites,  $f_{GB}^{\max}$ , depends on the prior austenite grain size,  $d_{\gamma}$ , and on the length of the bainite sub-unit,  $u_L$ . This maximum fraction is given by Eq. (15):

$$f_{GB}^{\max} = Z \frac{u_L}{d_{\gamma}} \quad (15)$$

where  $Z$  is a shape factor equal to 3.35 for a tetrakaidecahedron-shaped austenite grain [25].

Similar to  $f_{GB}^{\max}$ , the maximum fraction of bainite that can be formed by autocatalysis,  $f_A^{\max}$ , can be defined. However, unlike  $f_{GB}^{\max}$ ,  $f_A^{\max}$  varies during the transformation. At the beginning of the transformation, when no bainite is formed, it is not possible to have autocatalysis. Fig. 1b shows that after the first sub-unit of bainite is formed at the austenite grain boundary, new nucleation sites are created at the bainitic-ferrite/austenite interface, and autocatalysis can start. Considering that the first bainite sub-unit nucleated at the grain boundary can give rise to  $C_A$  bainite sub-units by autocatalysis, the change in  $f_A^{\max}$  promoted by a change in the fraction of bainite nucleated at the grain boundaries,  $f_{GB}$ , can be calculated by Eq. (16)

$$df_A^{\max} = C_A (1 - f_A^{\max}) df_{GB} \quad (16)$$

where  $df_A^{\max}$  is an infinitesimal change to  $f_A^{\max}$  induced by  $df_{GB}$ , an infinitesimal change to  $f_{GB}$ . The term  $(1 - f_A^{\max})$  is inserted to account for hard impingement. Integrating both sides of Eq. (16) with the boundary conditions of  $f_A^{\max} = 0$  for  $f_{GB} = 0$ , and  $f_A^{\max} = 1 - f_{GB}^{\max}$  for  $f_{GB} = f_{GB}^{\max}$  (Fig. 1c), results in Eq. (17) and (18):

$$C_A = \frac{\ln(f_{GB}^{\max})}{f_{GB}^{\max}} \quad (17)$$

$$f_A^{\max} = 1 - \exp\left(\frac{f_{GB}}{f_{GB}^{\max}} \ln f_{GB}^{\max}\right) \quad (18)$$

The boundary condition of  $f_A^{\max} = 1 - f_{GB}^{\max}$  when  $f_{GB} = f_{GB}^{\max}$  is not necessarily true. Sheaves of bainite may grow until they are halted by the austenite grain boundaries, such that the sheaves containing the plates marked as  $f_A$  in Fig. 1c actually occupy some of the area initially marked as  $f_{GB}^{\max}$ . The proposed boundary condition is then a simplification of a more complex problem, and it was chosen so that  $f_{GB}^{\max} + f_A^{\max}$  tends towards unity as the reaction progresses.

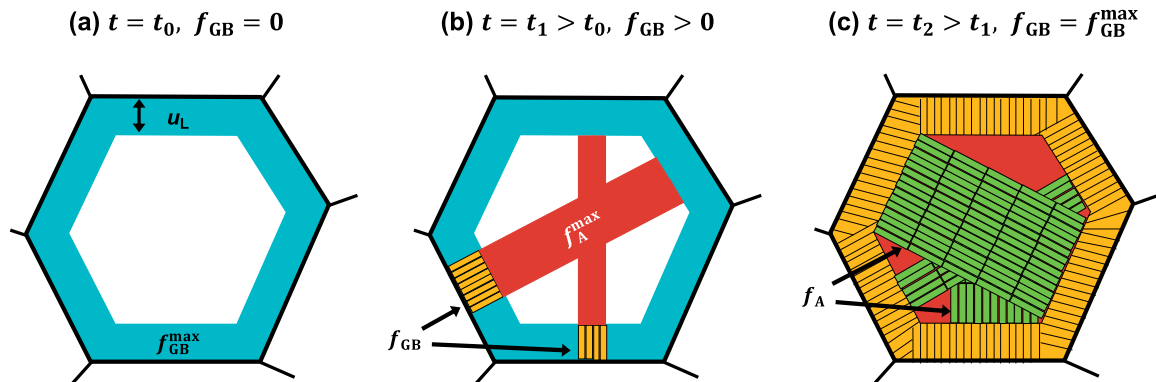


Fig. 1. Illustration representing the proposed geometrical assumption for bainite formation. A single austenite grain, at different times  $t$ , is shown. (a) The maximum fraction of bainite that can nucleate the austenite grain boundary,  $f_{GB}^{\max}$ , is given by the blue-shaded area, and is defined by the length of the bainite sub-unit,  $u_L$ , and the grain size. (b) After some fraction of bainite is formed by grain boundary nucleation, marked as  $f_{GB}$ , new plates of bainite can nucleate by autocatalysis and occupy the red-shaded area indicated by  $f_A^{\max}$ . (c) When  $f_{GB} = f_{GB}^{\max}$ , all the grain interior is available for transformation, such that  $f_{GB}^{\max} + f_A^{\max} = 1$ . The green plates indicated by the arrows and marked as  $f_A$  represent the fraction of bainite nucleated by autocatalysis at time  $t_2$ .



After having defined  $f_{GB}^{\max}$  and  $f_A^{\max}$ , the two terms can be combined with Eq. (13), which includes carbon enrichment of the austenite, and used for calculating the density of potential nucleation sites at the austenite grain boundaries,  $N_{tGB}$ , and at the bainite/austenite interfaces,  $N_{tA}$ , at any given time  $t$ , as

$$N_{tGB} = N_{S,GB} S_{GB} \left( 1 - \frac{f_{GB}}{f_{GB}^{\max}} \right) \left( \frac{T_0' - T}{T_{0X}' - T} \right) \quad (19)$$

$$N_{tA} = N_{S,A} S_A \left( 1 - \frac{f_A}{f_A^{\max}} \right) \left( \frac{T_0' - T}{T_{0X}' - T} \right) \quad (20)$$

where  $N_{S,GB}$  and  $N_{S,A}$  are respectively the number of potential nucleation sites per unit area of austenite grain boundary and bainite/austenite interface, later discussed in Section 4.1, and  $S_{GB}$  and  $S_A$  are the area of the austenite grain boundaries and bainite/austenite interfaces per unit volume, respectively. The autocatalytic nucleation of bainite is commonly considered to take place at the tip of previously formed bainitic ferrite sub-units [1]. Thus, instead of considering the whole bainite/austenite interface area for calculating  $S_A$ , only the interface area of the tip of the sub-units is considered. The terms can then be calculated as

$$S_{GB} = \frac{Z}{d_r} \quad (21)$$

$$S_A = \frac{f}{u_L} \quad (22)$$

While the concentrations of potential nucleation sites,  $N_{S,GB}$  and  $N_{S,A}$ , and the interface area of prior austenite grain boundaries,  $S_{GB}$ , are constant, the interface area of the sub-units tip,  $S_A$ , depends on the fraction of bainite existing at given time.

In order to calculate the rate of bainite nucleation, Eqs. (19) and (20) are used in Eqs. (5) and (7), changing the way in which Ravi et al. calculated the number density of potential nucleation sites.

By comparing Eqs. (19) and (20) with Eqs. (6), (8), and (13) it can be seen that in the proposed model the saturation of nucleation sites for grain boundary nucleation and autocatalysis are distinguished through the terms  $1 - f_{GB}/f_{GB}^{\max}$  and  $1 - f_A/f_A^{\max}$ . In Ravi's model, site saturation is treated as if it were equal for both grain boundary and autocatalysis, through the use of the single term  $1 - f$ .

### 2.3. Input parameters

Most of the input parameters needed for the model can be measured, calculated from empirical equations, or extracted from thermodynamic databases as described by Ravi et al. [18]. However, because of the modifications proposed here, four new input parameters are needed:  $N_{S,GB}$ ,  $N_{S,A}$ ,  $V_b$ , and  $u_L$ . Note that although  $V_b$  appears in the equations from Ravi et al. [18], it gets canceled out eventually (see Eqs. (5)–(8) and (14)). For the purpose of the present work, both  $N_{S,GB}$  and  $N_{S,A}$  were taken as  $10^{16} \text{ m}^{-2}$ , following van Bohemen [26].  $V_b$  is calculated as  $u_T \cdot u_W \cdot u_L$ , where  $u_T$  and  $u_W$  are the thickness and the width of the bainite sub-unit. In the present work, the sub-unit was considered to be a plate with  $u_W = u_L = 6 \cdot u_T$ , following Azuma et al. [27]. The values chosen for those parameters are discussed in Section 4.1. The fraction of carbon trapped in the bainite,  $X_b$ , and the activation energies,  $Q_{GB}$  and  $Q_A$ , are fitting parameters, as in Ravi et al.'s model.

## 3. Results

This section starts with a theoretical analysis of the model, focusing on the predicted influence of the prior austenite grain size on the bainite formation, and the differences with respect to the results obtained following the model developed by Ravi et al. [18]. Then, the model is validated by comparison against the experimental data.

### 3.1. Theoretical analysis of the model

The model was first theoretically analyzed by simulating kinetic curves of bainite formation using hypothetical input parameter values that result in realistic transformation rates. Then, the effect of prior austenite grain size was also theoretically studied for different model input parameter values. All the parameters used in the simulations of this section are given in the graphs and captions of Fig. 2 and Fig. 3.

Fig. 2 shows the simulated kinetics of bainite formation during isothermal holding. The simulated curve follows a sigmoidal-like shape, resembling the experimentally measured curves of bainite formation. Because the model distinguishes the fraction of bainite per nucleation site, the curves for bainite nucleated at the austenite grain boundaries and by autocatalysis can be calculated individually, as shown in Fig. 2a. The curve for  $f_{GB}$  follows a logarithmic shape approaching a limiting value. For the case presented in Fig. 2, since there is no carbon enrichment of the austenite ( $X_b = \bar{X}$ ), the limiting value for  $f_{GB}$  is given by  $f_{GB}^{\max}$ . The  $f_A$  curve, on the other hand, follows a sigmoidal-like shape. For the present case, in which there is no carbon enrichment,  $f_A$  approaches  $1 - f_{GB}^{\max}$ , so that the total fraction of bainite,  $f$ , tends towards unity.

Fig. 2b shows the rate of bainite formation distinguished by nucleation site. At the beginning of the transformation, the rate of bainite formation comes from grain boundary nucleation only. As the reaction progresses, potential nucleation sites are created at the bainite/austenite interface, and autocatalysis starts contributing to the total rate of bainite formation.

Many of the models that adopt the diffusionless theory of bainite formation use a so-called autocatalytic factor [18–20]. The autocatalytic factor,  $\lambda$ , is used to relate the rate of bainite nucleation at the grain boundaries,  $N_{GB} \dot{N}_{GB}$ , to the nucleation rate by autocatalysis,  $N_A \dot{N}_A$ , through the general expression  $N_A \dot{N}_A = \lambda f N_{GB} \dot{N}_{GB} = \lambda f \dot{N}_{GB}$ . In the present model, no autocatalytic factor was used. However, by isolating  $\lambda$  in the general formula present in other models, an autocatalytic factor can be derived and calculated using the outcome of the present model according to Eq. (23).

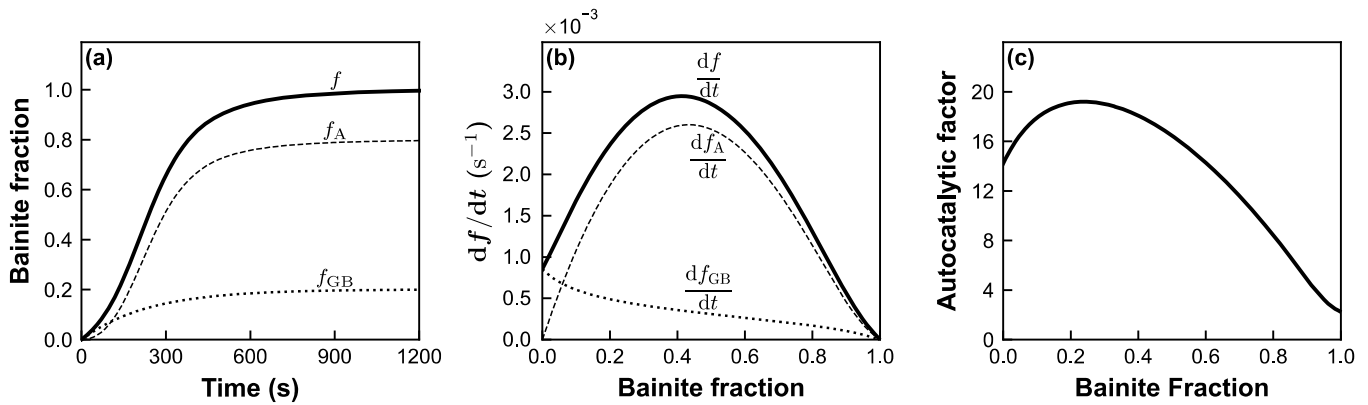
$$\lambda = \frac{1}{f} \frac{\dot{N}_A}{\dot{N}_{GB}} \quad (23)$$

The calculated autocatalytic factor is shown in Fig. 2c. Unlike in other bainite models, where it is usually taken as a value to be fitted, in the present model the autocatalytic factor is an outcome. The autocatalytic factor depends on the interplay between parameters such as the prior austenite grain size, size of the bainite sub-unit, and the difference between the activation energies  $Q_{GB}$  and  $Q_A$ , which in turn depends on the chemical composition, temperature, and dislocations created during bainite formation. Also, the factor is not constant, but varies throughout the whole transformation.

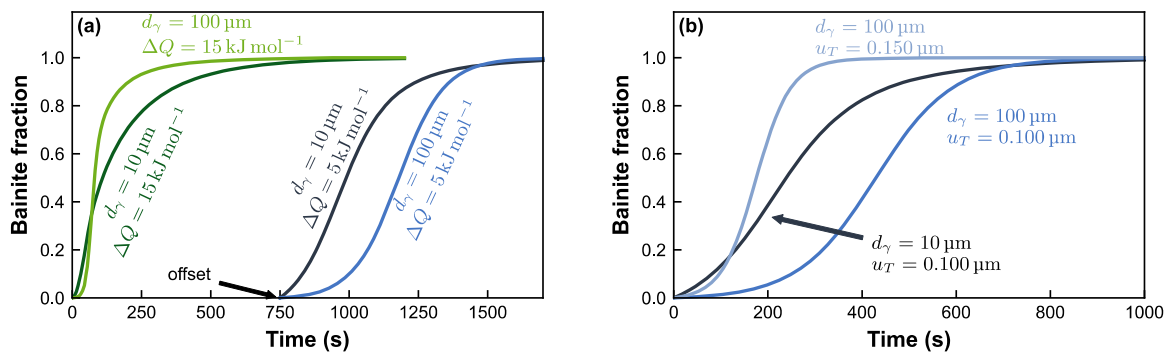
The predicted effect of the prior austenite grain size on the bainite formation kinetics is presented in Fig. 3. Depending on the difference between the activation energies for grain boundary and autocatalytic nucleation,  $\Delta Q = Q_{GB} - Q_A$ , and on the variation of the thickness of the bainite sub-unit as a function of the prior austenite grain size, different behaviors are observed.

When the activation energies  $Q_{GB}$  and  $Q_A$  were considered to differ by only  $5 \text{ kJ mol}^{-1}$ , a smaller grain size led to faster bainite formation. But when  $Q_A$  was smaller than  $Q_{GB}$  by  $15 \text{ kJ mol}^{-1}$ , a larger prior austenite grain size led to a faster bainite formation (see Fig. 3a). This indicates that as the difference  $\Delta Q$  between activation energies increases, the kinetics of bainite formation by autocatalysis tends to overcome the kinetics of bainite formation at austenite grain boundaries, ultimately leading to the observation of a faster bainite formation for larger prior austenite grain sizes.

In Fig. 3a,  $u_T$  was considered to be independent of the prior austenite



**Fig. 2.** Simulated kinetics of bainite formation considering the parameters:  $T = 300\text{ }^{\circ}\text{C}$ ,  $d_{\gamma} = 10\text{ }\mu\text{m}$ ,  $Q_{\text{GBx}^-} = 200\text{ kJ mol}^{-1}$ ,  $Q_{\text{Ax}^-} = 195\text{ kJ mol}^{-1}$ ,  $u_{\text{T}} = 0.100\text{ }\mu\text{m}$ , and  $X_{\text{b}} = X^-$ . (a) Fraction of bainite over time, distinguishing the total fraction,  $f$ , the fraction nucleated by autocatalysis,  $f_{\text{A}}$ , and the fraction nucleated at austenite grain boundaries,  $f_{\text{GB}}$ . (b) Rate of bainite formation, also showing the total rate and distinguishing individual components by nucleation site. (c) Autocatalytic factor calculated by Eq. (23).



**Fig. 3.** Simulated curves showing the predicted effect of varying the prior austenite grain size from 10 to 100  $\mu\text{m}$  on the bainite formation kinetics. The fixed parameters used were  $T = 300\text{ }^{\circ}\text{C}$ ,  $Q_{\text{GBx}^-} = 200\text{ kJ mol}^{-1}$ , and  $X_{\text{b}} = X^-$ , while  $\Delta Q$  ( $Q_{\text{GB}} - Q_{\text{A}}$ ) or  $u_{\text{T}}$  were varied. (a) On the left, simulated curves for  $\Delta Q = 15\text{ kJ mol}^{-1}$ . On the right and offset by 750 s, simulated curve for  $\Delta Q = 5\text{ kJ mol}^{-1}$ . In all cases,  $u_{\text{T}}$  was taken as 0.100  $\mu\text{m}$ . (b) Curves for  $\Delta Q = 5\text{ kJ mol}^{-1}$ . For  $d_{\gamma} = 10\text{ }\mu\text{m}$ ,  $u_{\text{T}} = 0.100\text{ }\mu\text{m}$ . For  $d_{\gamma} = 100\text{ }\mu\text{m}$ , two curves are shown: one considering the thickness of the sub-unit does not change by varying the grain size, and one considering that because of the increase in grain size the thickness of the sub-unit increases to 0.150  $\mu\text{m}$ .

grain size. But in reality  $u_{\text{T}}$  might be different for different austenite grain sizes. In the present model, the nucleation rate is multiplied by the volume of the sub-unit to yield the rate of bainite formation, and thus a larger sub-unit speeds up the transformation. This possibility was explored in the simulation shown in Fig. 3b.

In Fig. 3b, the two curves from Fig. 3a corresponding to  $\Delta Q = 5\text{ kJ mol}^{-1}$ , for which smaller austenite grains led to a faster transformation, are shown again and complemented by a third simulated curve. In the latter, it is considered that by increasing the prior austenite grain size from 10 to 100  $\mu\text{m}$  the thickness of the sub-unit increases from 0.100 to 0.150  $\mu\text{m}$ . As a result, the effect of the grain size was reversed, and a larger prior austenite grain size resulted in a faster overall bainite formation.

The theoretical analysis described in this section indicates that the proposed model is capable of reproducing both the acceleration as well as the deceleration of bainite formation by the refinement of the prior austenite grain size. To our knowledge, and based on our analysis of other published models of bainite formation [18,20,27–29], the model proposed here is the only one that is able to simulate these two possible effects.

None of the results shown in this section considered the carbon enrichment of the austenite. However, we have repeated the simulations considering the carbon enrichment of austenite by choosing different values for  $X_{\text{b}}$  (section S1 and Fig. S1 to S3 in the supplementary materials) and we did not find any influence of the carbon enrichment of the austenite on the effect of the prior austenite grain size on bainite

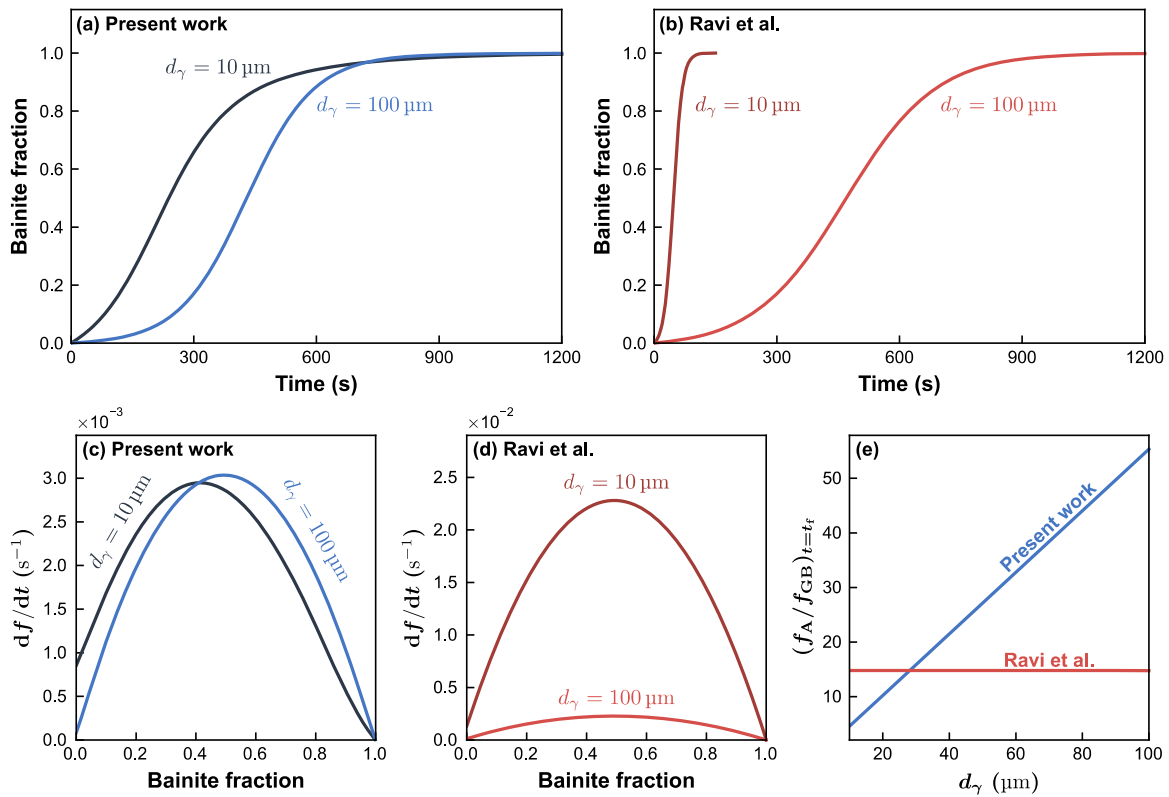
formation kinetics.

### 3.2. Comparison to Ravi et al.'s model

The predicted effect of the prior austenite grain size was also analyzed for Ravi et al.'s model, and a comparison between their model and the model from the present work is shown in Fig. 4. The simulations presented in this section use parameters similar to the ones used in Section 3.1 for the proposed model, and parameters for Ravi et al.'s model that led to similar kinetics. All parameters and values are given in the graphs and caption of Fig. 4.

By comparing Fig. 4a and c with Fig. 4b and d, it is evident that the model from Ravi et al. predicts a much greater influence of the prior austenite grain size on the kinetics of bainite formation. In the present model, the effect of grain size depends on factors such as the difference in the activation energies and the size of the bainite sub-unit. Fig. 4a and c thus represent only the specific case for the conditions used in the simulation. In Ravi et al.'s model, the rate of bainite formation is always inversely proportional to the prior austenite grain size, given that the activation energies are independent of the grain size. Hence, the trends shown in Fig. 4b and d are general for Ravi et al.'s model, and it is the only possible outcome, irrespective of the parameters used in the simulation.

As the rate of bainite nucleation at grain boundaries and by autocatalysis are distinguished in both models, it is possible to calculate the final fraction of grain boundary nucleated and autocatalytically



**Fig. 4.** Effect of the prior austenite grain size on bainite formation according to the present model and Ravi et al.'s model. In all cases  $T = 300\text{ }^{\circ}\text{C}$  and  $X_b = X^-$  were considered. For the simulations using the model from the present work,  $Q_{GBx^-} = 200\text{ kJ mol}^{-1}$ ,  $Q_{Ax^-} = 195\text{ kJ mol}^{-1}$ , and  $u_T = 0.100\text{ }\mu\text{m}$  were used. In the simulations using Ravi et al.'s model,  $Q_{GBx^-} = 145\text{ kJ mol}^{-1}$ ,  $Q_{Ax^-} = 125\text{ kJ mol}^{-1}$ ,  $T_h = 577\text{ }^{\circ}\text{C}$ , and  $\alpha_m = 0.011\text{ K}^{-1}$  were used. (a–d) Simulated bainite fraction as a function of time and the rate of bainite formation as a function of bainite fraction for both models and for  $d_\gamma = 10\text{ }\mu\text{m}$  and  $d_\gamma = 100\text{ }\mu\text{m}$ . (e) Ratio between the fraction of autocatalytic nucleated and grain boundary nucleated bainite at the end of the transformation as a function of prior austenite grain size for both models.

nucleated bainite at the end of the transformation, and then calculate their ratio. Fig. 4e shows this ratio as a function of the prior austenite grain size for both models. For the model developed in the present work, the ratio increases linearly with the prior austenite grain size, meaning that autocatalysis becomes more important for larger austenite grains. On the other hand, in the model from Ravi et al., the ratio is constant with respect to the austenite grain size.

The linear relationship observed in Fig. 4e was achieved in the present model by the introduction of the parameters  $f_{GB}^{\text{max}}$  and  $f_A^{\text{max}}$ , both a function of the prior austenite grain size and the length of the bainite sub-unit. The linearity is a direct consequence of the assumption that  $f_{GB}$  at the end of the transformation is proportional to the interface area of the prior austenite grain boundaries,  $S_{GB}$ , which in turn is inversely proportional to the prior austenite grain size,  $d_\gamma$  – Eq. (15) and (21). Such a relationship is derived in section S2 of the supplementary materials. The two parameters control the relative contribution of grain boundary nucleation and autocatalysis, and also limit their overall fraction. In the model from Ravi et al., on the other hand, there is no limit on the fraction of grain boundary nor autocatalytic nucleated bainite, and their relative contribution does not depend on the austenite grain size nor on the bainite sub-unit size. In Ravi et al.'s model, at any given point of the transformation, the ratio between the nucleation rates is

$$\frac{df_A/dt}{df_{GB}/dt} = f \exp\left(\frac{\Delta Q}{RT}\right) \quad (24)$$

which shows that the relative contribution of each type of nucleation site is determined solely by the difference in the activation energies, and does not include the effect of the prior austenite grain size.

### 3.3. Comparison against experiments

Experimental data on the kinetics of bainite formation during isothermal holding measured by dilatometry was used to validate the present model. The chemical composition, prior austenite grain size, isothermal holding temperature, thickness of the bainite sub-unit and references to the original source of the data are in Table 1, alongside the given nomenclature. The curves of bainite fraction as a function of time were used for optimizing the fitting parameters ( $Q_{GBx^-}$ ,  $Q_{Ax^-}$ , and  $X_b$ ), and the implementation of the differential evolution algorithm [30] in SciPy and Lmfit [31,32] was used to find the best values.

In order to investigate the effect of the transformation temperature, Steels A and B, which were treated at holding temperatures in the range of 370 to 500  $^{\circ}\text{C}$ , were first fitted to the model. Fig. 5a and b show that the present model was able to match well the experimentally observed data for both steels and at every temperature. The activation energies extracted from the fitting are shown in Fig. 5c and d and listed in Table 1, and range from 220 to 270  $\text{kJ mol}^{-1}$ . Both  $Q_{GBx^-}$  and  $Q_{Ax^-}$  increase linearly with the temperature.

The optimal fitted values for the activation energies bear uncertainties related to the fitting procedure itself and to the uncertainty in the input parameters. The uncertainty related to the fitting procedure is relatively small and estimated as less than 0.1  $\text{kJ mol}^{-1}$ . The uncertainty related to the input parameters, however, is much higher. By assuming there is a 10% uncertainty in the values for the prior austenite grain size and for the sub-unit thickness, and a 50% uncertainty in the sub-unit aspect ratio, the uncertainty for  $Q_{GBx^-}$  and  $Q_{Ax^-}$  were estimated as 4% and 2%, respectively. The estimation of the uncertainty in the activation energies is detailed in section S3 of the supplementary materials.

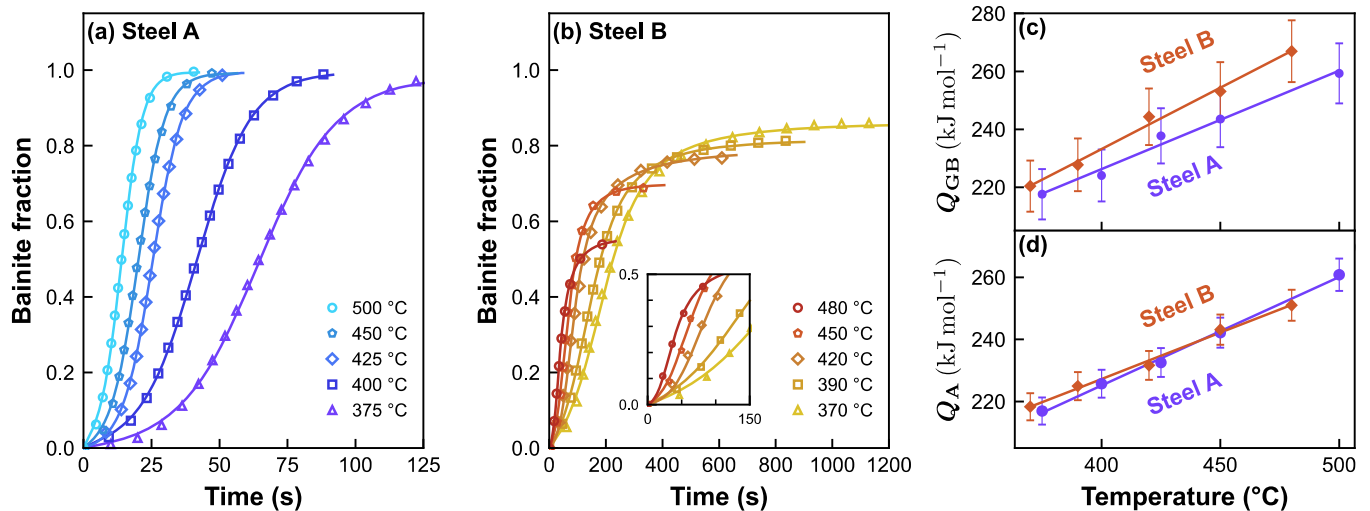
Steels C and D were chosen for analyzing the effect of the prior



**Table 1**

Chemical composition, prior austenite grain size ( $d_i$ ), temperature of bainite formation ( $T$ ), thickness of the bainite sub-unit ( $u_T$ ), and model outputs ( $Q_{GBx^-}$ ,  $Q_{Ax^-}$ , and  $X_b$ ) of the steels used for the validation. The grain size of steel A is not reported in the original paper [29] and thus the value estimated by [20] is used. The thickness of the bainite sub-unit for steels A and B were not reported, and thus were calculated using the model from [33] for steel A and from [34] for steel B.  $Q_{GBx^-}$ ,  $Q_{Ax^-}$  and  $X_b$  result from fitting the data to the model and assuming that  $Q_{GBx^-}$  and  $Q_{Ax^-}$  are independent of  $d_i$ .

Steel	Ref.	Chemical composition wt.%	$d_i$ $\mu\text{m}$	$T$ $^{\circ}\text{C}$	$u_T$ $\mu\text{m}$	$Q_{GBx^-}$ $\text{kJ mol}^{-1}$	$Q_{Ax^-}$ $\text{kJ mol}^{-1}$	$X_b$ at. frac.
A	[29]	Fe-0.53C-0.69Mn-0.29Cr-0.03Al	140	500	0.327	259	261	0.0241
			140	450	0.260	244	242	0.0241
			140	425	0.227	238	232	0.0241
			140	400	0.194	224	225	0.0241
			140	375	0.160	218	217	0.0240
B	[35]	Fe-0.29C-2.39Mn-1.76Si	22	480	0.178	267	251	0.0060
			22	450	0.152	253	243	0.0077
			22	420	0.131	244	232	0.0089
			22	390	0.113	228	225	0.0086
			22	370	0.102	220	218	0.0096
C	[16]	Fe-0.25C-1.6Mn-1.25Si-1Cr-0.3Mo	16	420	0.255	259	243	0.0114
			20	420	0.296	259	243	0.0096
			76	420	0.353	259	243	0.0079
			157	420	0.416	259	243	0.0075
D	[14]	Fe-0.51C-0.83Mn-1.72Si-0.98Cr-0.25Mo-0.56Co-0.60Ni-0.04Nb	33	280	0.297	202	200	0.0068
			50	280	0.297	202	200	0.0068
			72	280	0.297	202	200	0.0068
			93	280	0.297	202	200	0.0068



**Fig. 5.** Model fitted to the experimental data from steels A and B for several different holding temperatures. In (a) and (b) the markers represent the experimental data and the lines represent the fitted model. Markers in (c) and (d) show the initial activation energies extracted from the fit for Steel A (purple circle) and Steel B (red diamond), while the solid lines show linear fits. The error bars in (c) and (d) were calculated considering an uncertainty of 10% in  $d_i$  and in  $u_T$ , and 50% in the aspect ratio of the bainite sub-unit.

austenite grain size because they show opposite behaviors. In the case of Steel C, bainite formation was accelerated by increasing the prior austenite grain size, while for Steel D the reaction was accelerated by decreasing the grain size. For each steel, samples with different grain sizes were treated isothermally at the same holding temperature.

Fig. 6 shows the experimental and modelled fraction of bainite as a function of time for the steels C and D. Because all treatments for a given steel were performed at the same holding temperature, the values of  $Q_{GBx^-}$  and  $Q_{Ax^-}$  were fitted considering that they are the same irrespective of the prior austenite grain size. The modelled curves were able to reproduce the opposing effects of the austenite grain size seen in both steels.

In the case in which bainite formation was faster for a larger prior austenite grain size (Steel C, Fig. 6a), the activation energy for grain boundary nucleation was  $16 \text{ kJ mol}^{-1}$  higher than the activation energy for autocatalytic nucleation. For Steel D (Fig. 6b), which shows the opposite effect, the difference between the activation energies was only  $2 \text{ kJ mol}^{-1}$ . This can be taken as an indication that the lengthening of

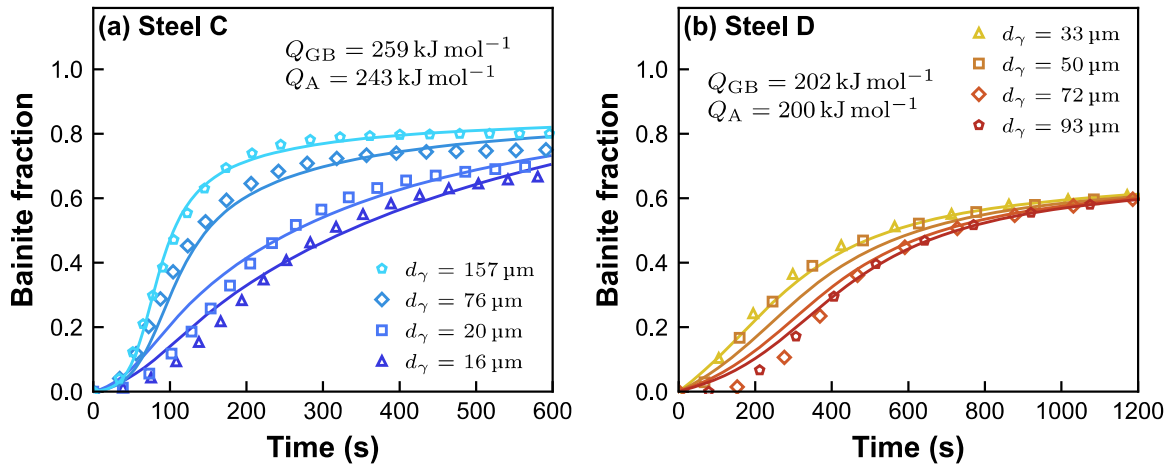
bainite sheaves by the successive nucleation of bainite sub-units is relatively faster than their nucleation at grain boundaries for Steel C than it is for Steel D. This result also matches the predictions from the simulations described in Fig. 3 and the experimental observations made by Matsuzaki and Bhadeshia [9].

## 4. Discussion

### 4.1. Model parameters

#### 4.1.1. Size of the bainite sub-unit

Both the length and the volume of the bainite sub-unit are an integral part of the present model. Their values are, however, difficult to measure. On the other hand, the thickness of the sub-units have been extensively measured and can be estimated using empirical equations available in the literature [33,34]. Then, the length can be calculated by assuming an aspect ratio – which is, however, also difficult to estimate. Based on the images from Bhadeshia et al. [37], the size of a sub-unit



**Fig. 6.** Experimental data (markers) and modeled curve (solid line) of bainite formation for (a) steel C and (b) steel D at different prior austenite grain sizes, alongside the best fit values for the initial activation energies. Since the retained austenite fraction for Steel D was not reported, it was estimated using the steel models from Thermo-Calc version 2023a with the thermodynamic database TCFE12 [36].

was estimated to be  $0.2 \times 10 \times 10 \mu\text{m}$ , which indicates an aspect ratio of 50. In-depth analysis at a higher resolution indicated that the aspect ratio could actually be in the range from 2 to 15 [38–40]. All of these values are based on a few images from transmission electron microscopy, and thus should be interpreted with care. Also, the size of the sub-unit should not be mistaken for the size of a sheaf of bainite seen by optical microscopy [41], since a sheaf is an aggregate of several individual sub-units.

Azuma et al. [27] were able to model the change from upper to lower bainite assuming an aspect ratio of 6, a value that lies in the middle of the 2 to 15 range. For that reason, the aspect ratio was assumed to be 6 in the present work. Since this estimate bears much uncertainty, and may vary depending on the chemical composition of the steel and the transformation temperature, a 50% uncertainty on the aspect ratio was considered when calculating the errors in  $Q_{GBx^-}$  and  $Q_{Ax^-}$ .

The rate of bainite formation is proportional to the volume of the bainite sub-unit in the present model. Although this differs from Ravi et al.'s model [18], in which  $V_b$  has no influence, it is in line with other models of bainite formation, such as the one from Matsuda and Bhadeshia [42]. Given that a higher  $V_b$  means that each nucleation event will give rise to a correspondingly greater fraction of bainite, it seems reasonable to assume this linear relationship.

Correctly capturing the influence of the volume of the sub-unit on the rate of bainite formation is especially important in the present work because by changing the prior austenite grain size the volume of the sub-unit may also change. And, in turn, the correlation between  $V_b$  and  $d_\gamma$  could define the effect of the prior austenite grain size on the kinetics of bainite formation, as shown in the simulation presented in Fig. 3b. This relation between  $V_b$ ,  $d_\gamma$ , and the kinetics of bainite formation will be further discussed in Section 4.2.

#### 4.1.2. Density of potential nucleation sites

According to the displacive theory of bainite formation, nucleation happens by the dissociation of dislocations, similar to martensite formation [1,43]. Because of this similarity, Magee's work on martensite nucleation [23] was used by van Bohemen [20] in order to estimate the density of initially present potential nucleation sites for bainite.

In the case of martensite, Magee assumed that there is a linear relationship between the driving force for the fcc  $\rightarrow$  bcc transformation and the number of nucleation events of new martensite plates per unit volume of austenite. Following this simple assumption, Magee arrived at the same expression relating undercooling and fraction of martensite than the one found empirically by Koistinen and Marburger [44]. At small undercoolings below  $M_s$ , the number of martensite plates

nucleated per unit volume of austenite is calculated as

$$N_m = \frac{\alpha_m}{V_m} (M_s - T) \quad (25)$$

where  $N_m$  is the number of martensite plates per unit volume of austenite,  $V_m$  is the average volume of martensite plates, and  $M_s$  is the martensite start temperature.

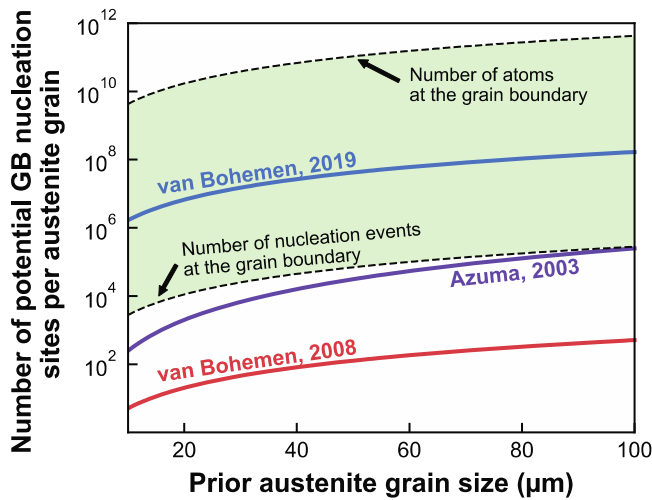
While martensite seems to nucleate in defects present inside the austenite grains, bainite seems to nucleate preferentially at the austenite grain boundaries. Thus, in order to calculate the potential nucleation sites for bainite, van Bohemen [20] scaled down Eq. (25) by the factor  $6\delta/d_\gamma$  and changed the martensite-related parameters  $M_s$  and  $V_m$  by the corresponding bainite-related parameters  $T_h$  and  $V_b$ , giving rise to Eq. (6), which is also used in Ravi et al.'s model [18]. There are two factors, however, that could lead to errors in van Bohemen's [20] approach.

First, in Magee's derivation of the Koistinen-Marburger, Eq. (25), it is not the density of initially present potential nucleation sites that is calculated, but the density of plates of martensite that actually nucleate. When a potential nucleation site is activated, a plate of martensite nucleates and then grows to its final size, sweeping many other potential nucleation sites in the process. Thus, the real number of potential nucleation sites may be much higher than the number of plates that actually nucleate, and the two values should not be equated.

Also, the effect of autocatalysis has been overlooked in van Bohemen's derivation. Since Magee's equation considers the total number of martensite plates nucleated, it takes into account not only the martensite plates nucleated at pre-existing defects in austenite but the plates nucleated by autocatalysis at newly created nucleation sites (for more detail see Fig. 2 in [23]). But when adapting it to the case of bainite nucleation at defects initially present in the austenite, Eq. (25) was used as if it concerned only nucleation at pre-existing defects and did not include autocatalysis – which is not the case.

Different approaches were used in other bainite models, mostly using the density of potential nucleation sites at the austenite grain boundaries,  $N_{S,GB}$ , as a fitting parameter [26,27,29,42,45–49]. The values reported differ by a striking 46 orders of magnitude, varying from  $10^{-30}$  [48] to  $10^{16}$  per  $\text{m}^2$  of austenite grain boundary [26]. The wide range may be partially caused by the difficulty of simultaneously fitting the activation energy and the density of potential nucleation sites.

In order to perform a quantitative analysis, the values of  $N_{S,GB}$  were compared to the physically-based limits – calculated for a single austenite grain – that we propose in Fig. 7. Considering that nucleation of bainite plates at the austenite grain boundaries takes place at pre-existing defects, the number of potential nucleation sites initially



**Fig. 7.** Potential sites for bainite nucleation per austenite grain as a function of grain size calculated according to the models from van Bohemen, 2008 [20], Azuma [27] and van Bohemen, 2019 [26]. The calculations were performed considering  $u_T = 0.100 \mu\text{m}$ ,  $u_W = u_L = 0.600 \mu\text{m}$ ,  $T_h - T = 100 \text{ K}$ ,  $\alpha_m = 0.011 \text{ K}^{-1}$ ,  $Z = 3.35$ , and  $2.5 \cdot 10^{19}$  atoms per  $\text{m}^2$  of austenite grain boundary. The shaded area marks the region limited at the bottom by the number of nucleation events at the grain boundary necessary to occupy the whole austenite grain boundary and at the top by the number of atoms in the austenite grain boundary.

present should be *at least* as large as the number of nucleation events necessary to fully occupy the austenite grain boundary. The number of necessary nucleation events can be calculated by dividing the grain boundary area by the bainite sub-unit tip area. The *upper limit* for the potential nucleation sites is the number of atoms present at the austenite grain boundary.

Fig. 7 shows that the values reported by van Bohemen in 2019 [26], at  $N_{S,GB} = 10^{16} \text{ m}^{-2}$  and at the top of the observed range, are the only ones that lie inside the range given by the proposed limits. The early values found by van Bohemen in 2008 [20], Eq. (6), and used by Ravi et al. [18] and subsequent models [50,51] are three to four orders of magnitude smaller than the lower limit. The curves for most of the other cited models are not shown in Fig. 7 because they are too far from the limiting range, with most resulting in less than one potential nucleation site per austenite grain.

From the above discussion it is clear that estimating  $N_{S,GB}$ , either by using it as a fitting parameter or by relating it to martensite nucleation, is not straightforward. Also, the physical interpretation of the density of potential nucleation sites and the enormous discrepancy among the reported values have been overlooked in previous models of bainite nucleation. In the present work,  $N_{S,GB}$  was taken as  $10^{16} \text{ m}^{-2}$ , following van Bohemen [26], because it is the only value reported so far that is within the limits shown in Fig. 7. Additionally, this value, which is equivalent to one potential nucleation site every  $100 \text{ nm}^2$  of austenite grain boundary, is consistent with the mechanism of bainite nucleation proposed by the displacive-diffusionless theory of bainite formation [1].

Considering that bainite nucleation is similar to that of martensite, the controlling mechanism is then the dissociation of dislocations. Although the structure of grain boundaries is not always well defined, it can be sometimes well represented in terms of arrays of dislocations or similar defects [52] separated by a few atomic distances [53]. The separation of these defects is in line with the density of potential nucleation sites used in the present work. Then, a similar argument can be made for nucleation at the tip of the bainite sub-units,  $N_{S,A}$ , which in the present work was also taken as equal to  $10^{16} \text{ m}^{-2}$ .

The initial density of potential nucleation sites for a steel with a prior austenite grain size of  $50 \mu\text{m}$ , considering  $N_{S,GB}$  as  $10^{16} \text{ m}^{-2}$ , is in the order of  $10^{20}$  to  $10^{21} \text{ m}^{-3}$ . Although it is physically consistent with the

argument made in Fig. 7, it is much higher than the values reported for martensite. Based on classical small particles experiments, the density of initially-present potential nucleation sites for martensite was estimated as  $10^{11}$  to  $10^{13} \text{ m}^{-3}$  [23].

In the case of martensite, however,  $10^{11}$  to  $10^{13}$  initial potential nucleation sites per  $\text{m}^{-3}$  is enough to ensure a full transformation. This is because the volume of martensite plates can be much higher than that of bainite plates, and the creation of new potential sites for nucleation by autocatalysis is much higher for martensite than for bainite. While the autocatalytic factor for bainite is usually in the order of 3 to 200 [20,28], for martensite it is reported to be in the range of 1000 [23,54,55]. Also, the fact that martensite formation is seen to start in the grain interiors and bainite formation in the grain boundaries indicates that, despite their mechanism of formation being similar, their nucleation sites are not exactly the same.

Finally, given the uncertainty in the values of  $N_{S,GB}$  and  $N_{S,A}$ , it is important to know their effect in the model. Both values multiply the exponential term containing the activation energies for nucleation. Since the activation energies are fitted to the experimental data, any error in the density of potential nucleation sites results in an erroneous estimation of the activation energy – an overestimation of  $N_{S,GB}$  leads to an overestimation of  $Q_{GB}$ , for instance. Since in all cases the same values of  $N_{S,GB}$  and  $N_{S,A}$  were used, any error in the assumed values resulted in roughly the same error in all values of  $Q_{GB}$  and  $Q_A$  extracted from fitting. This means that although the absolute values of  $Q_{GB}$  and  $Q_A$  reported in the present work bear this uncertainty with it, none of the trends – such as the ones in Fig. 5 and Fig. 6 – are affected by this uncertainty.

#### 4.1.3. Activation energy

The activation energies for bainite nucleation for steels A-D were found to be in the range from 200 to 270  $\text{kJ mol}^{-1}$ . These values are higher than the ones reported in previous models, which usually range from 100 to 180  $\text{kJ mol}^{-1}$  [18,20,42]. For steel A and B, the activation energies reported by Ravi et al. [18] were up to 120  $\text{kJ mol}^{-1}$  lower than the ones found in the present work. This difference is due to the underestimation of the density of potential nucleation sites in previous models.

In Eq. (5) and (7), the density of potential nucleation sites multiplies the exponential term containing the activation energy for nucleation. Hence, the activation energy found by fitting the model to experimental curves of bainite formation kinetics depends on the assumed density of potential nucleation sites. In the present work, we took the number of potential nucleation sites per interface area,  $N_{S,GB}$  and  $N_{S,A}$ , to be  $10^{16} \text{ m}^{-2}$ . Although we have explained that the assumed values are the most realistic considering the physical conditions of the transformation, here we further explore the consequences of using other values of  $N_{S,GB}$  and  $N_{S,A}$  in the resulting activation energies.

Fig. 8 shows the activation energy for bainite nucleation found for steel B isothermally treated at  $420 \text{ }^\circ\text{C}$  as a function of the assumed  $N_{S,GB}$  and  $N_{S,A}$ , which were varied from  $10^6$  to  $10^{16} \text{ m}^{-2}$ . Both  $Q_{GB}^-$  and  $Q_{Ax}^-$  vary by 130  $\text{kJ mol}^{-1}$  within this range. At  $10^{10}$  potential nucleation sites per  $\text{m}^{-2}$ , which is the order of magnitude used by Ravi et al.,  $Q_{GB}^-$  and  $Q_{Ax}^-$  are respectively 165 and 152  $\text{kJ mol}^{-1}$ , differing only by 3  $\text{kJ mol}^{-1}$  from the values found by Ravi et al. (168 and 155  $\text{kJ mol}^{-1}$ ). Thus, the lower values of activation energy for bainite previously reported in other models in the literature are a consequence of such models may having underestimated the density of potential nucleation sites for bainite nucleation.

According to the displacive theory of bainite formation, there are two thermally-activated events involved in the nucleation: carbon diffusion and dissociation of dislocations [1]. The activation energy for bainite nucleation,  $Q$ , can then be understood as the sum of the individual activation energies for carbon diffusion,  $Q_D$ , and for the dissociation of dislocations,  $Q^*$  [27,56]. Rigorously,  $Q_D$  is the activation energy for a carbon atom to jump from a bainite embryo to the austenite matrix. Since this value is not known,  $Q_D$  can be approximated as the activation

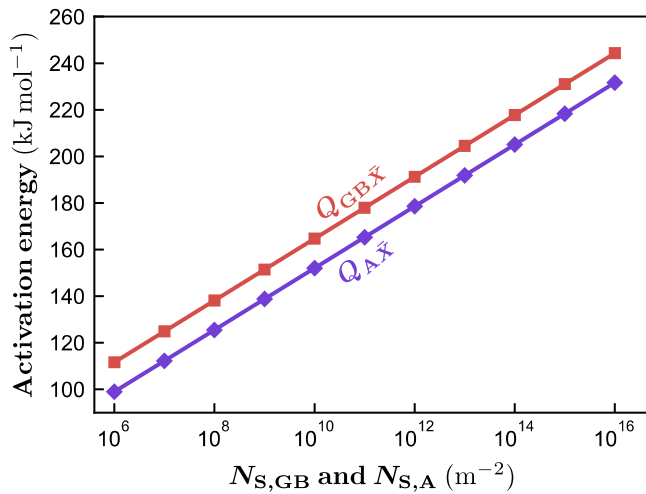


Fig. 8. Estimated activation energies for bainite nucleation in steel B isothermally treated at 420 °C as a function of the assumed values of the number of potential nucleation sites per interface area,  $N_{S,GB}$  and  $N_{S,A}$ .

energy for carbon diffusion in the austenite, which is around 140 kJ mol<sup>-1</sup> (from databases TCFE12 and MOBFE7 in Thermo-Calc). Thus,  $Q^*$  was found to vary from 60 to 130 kJ mol<sup>-1</sup>, which is smaller than the activation energy for the diffusional movement of ferrite/austenite interfaces, estimated as 140 kJ mol<sup>-1</sup> [57].

According to Olson and Cohen's theory of martensite nucleation [58], which has been adopted in the theory of bainite nucleation [1],  $Q^*$  can be calculated as

$$Q^* = Q_0^* + \left( \tau_\mu + \frac{\rho_A E_{str}}{b} + \frac{2\sigma}{nb} \right) v^* + \left( \frac{\rho_A v^*}{b} \right) \Delta G_m \quad (26)$$

where  $Q_0^*$  is the activation energy for overcoming the short-range barriers to dislocation movement,  $\tau_\mu$  is the athermal resistance to dislocation movement,  $\rho_A$  is the number of atoms per unit area of the closed packed plane,  $b$  is the Burgers vector,  $E_{str}$  is the strain energy,  $\sigma$  is the bainite/austenite interfacial energy,  $n$  is the number of atomic planes of the embryo, and  $v^*$  is the activation volume [1,58,59].

Since Eq. (26) has several unknown parameters ( $Q_0^*$ ,  $\tau_\mu$ ,  $E_{str}$ ,  $\sigma$ ,  $n$ ,  $v^*$ ), it cannot be directly used to calculate  $Q^*$ . The derivative of Eq. (26) with respect to temperature, however, can be used to estimate the activation volume for bainite nucleation. If  $\Delta G_m$  is assumed to be the only temperature-dependent parameter in Eq. (26), then the derivative is calculated as

$$\frac{dQ^*}{dT} = \frac{\rho_A v^*}{b} \frac{d(\Delta G_m)}{dT} \quad (27)$$

Using the values of  $\Delta G_m$  calculated in Thermo-Calc, the activation volume  $v^*$  for the grain boundary and autocatalytic nucleation of bainite in steel A is estimated as 55 and 57  $\Omega$ , respectively, and in steel B as 72 and 51  $\Omega$ , where  $\Omega$  is the atomic volume of the Fe atom ( $8.5 \cdot 10^{-30}$  m<sup>3</sup>). These values are in line with the range reported by Olson and Cohen for the isothermal martensite nucleation in Fe-Ni and Fe-Ni-Mn alloys, which was from 21 to 73  $\Omega$  [58].

The slopes  $dQ^*/dT$  for steels A and B, calculated from the curves shown in Fig. 5c and d, were in the range from 272 to 386 J K<sup>-1</sup>. Again, these values are close to those reported for isothermal martensite nucleation in Fe-Ni-Mn alloys, which were around 300 to 360 J K<sup>-1</sup> [54, 55].

#### 4.1.4. Lengthening rate of sheaves

A sheaf of bainite is a structure formed by an aggregate of bainite sub-units that were nucleated one at the tip of the other by autocatalysis. The lengthening of bainite sheaves is not, according to the diffusionless

theory, a continuous process, but rather a succession of several nucleation events. Although the present model is based on the individual nucleation events, the lengthening rate of bainite sheaves can be derived and compared with experimental values.

The apparent lengthening rate of a sheaf of bainite,  $v_L$ , can be calculated as the product of the length of a bainite sub-unit and the nucleation rate at the tip of a single sub-unit.

$$v_L = u_L \frac{kT}{h} N_{S,A} u_T u_W \exp\left(-\frac{Q_A}{RT}\right) \quad (28)$$

In Eq. (28), the product  $N_{S,A} \cdot u_T \cdot u_W$  is the number of potential nucleation sites at the tip of a single bainite sub-unit.

Fig. 9 shows the lengthening rate for steel A and B calculated using the model from the present work, the model from Ravi et al., and Thermo-Calc [60]. In Ravi's model  $N_{S,A}$  is not defined, and thus the number of potential nucleation sites at the tip of the individual sub-units cannot be calculated. However, for the bainitic transformation to progress, it is necessary to have at least one potential nucleation site at the tip of every sub-unit. For that reason, the term  $N_{S,A} \cdot u_T \cdot u_W$  was considered to be equal to one when calculating the lengthening rate according to Ravi's model. According to the model from the present work, the number of potential nucleation sites at the tip of the bainite sub-units varied from 600 to 6000 for Steels A and B.

The lengthening rates obtained for steel A and B using the present model were in the range from  $10^{-8}$  to  $10^{-6}$  m s<sup>-1</sup>. In comparison, using Ravi et al.'s model, lengthening rates up to  $10^{-2}$  m s<sup>-1</sup> were found, which is two orders of magnitude above the highest value reported in literature [1,60]. The unrealistically high values from Ravi et al.'s model are due to the underestimation of potential nucleation sites. Although one potential nucleation site per bainite sub-unit was assumed in the present calculation, the values of  $N_{iA}$  calculated from Eq. (8) suggest that in Ravi et al.'s model there is less than one potential nucleation site per tip of bainite sub-unit. This value is too low, since without at least one potential nucleation site per tip, the growth of a sheaf cannot progress.

For steel B, the lengthening rates calculated using the present model and using Thermo-Calc match well. For steel A, however, the rates calculated using the present model were 10 to 20 times lower. The results from Thermo-Calc simulation are closer to experimental values of steels with chemical composition similar to the one of steel B [60],

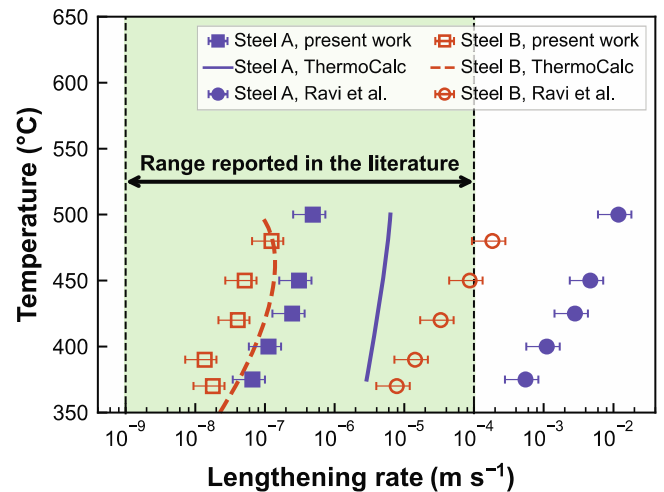


Fig. 9. Lengthening rate of bainite sheaves in steel A and B calculated according to the model from the present work, to the model from Ravi et al. [18], and to Thermo-Calc [36,60]. Shaded area represents the range of values reported in the literature so far for several steels [1,60]. The error bars were estimated considering an uncertainty of 10% in  $d_v$  and in  $u_T$ , and 50% in the aspect ratio of the bainite sub-unit. The error associated with the Thermo-Calc could not be estimated, but based on Ref. [60] it may span more than one order of magnitude.



indicating that the present model underestimated the lengthening rate of the bainitic sheaf. However, two critical aspects need to be considered when making this comparison.

First, the model from the present work and Thermo-Calc's model use different optimization strategies. While Thermo-Calc's model used for calculating the curves in Fig. 9 was optimized to match the experimentally measured lengthening rates [60], the model from the present work was optimized to match the overall kinetics of bainite formation. Even so, the difference between Thermo-Calc's simulation and the experimentally measured lengthening rates can differ by a factor of 20 [60].

Second, the experimental data used for optimizing Thermo-Calc's model was measured either by in situ hot-stage microscopy or by measuring the longest bainite sheaf after interrupted transformation. The former technique measures the lengthening rate on the surface, which can be faster than in the bulk because of free surface effects [60]. The later technique measures the rate of the fastest growing sheaf, not the average lengthening rate.

#### 4.2. Effect of the prior austenite grain size on bainite formation

Refining the grain size of the parent phase usually accelerates the formation of the precipitating phase. In the case of bainite, not only acceleration but deceleration have been reported. In the present work, both behaviors were successfully replicated by a single model, as shown in Fig. 3 and Fig. 6. In the model developed, the behavior that the steel will show depends on  $\Delta Q$  – the difference between the activation energy for grain boundary and autocatalytic nucleation – and on how the thickness of the bainite sub-unit,  $u_T$ , varies with the prior austenite grain size.

The effect of  $\Delta Q$  has been verified experimentally by Matsuzaki and Bhadeshia [9], who analyzed the microstructure after interrupted bainitic treatment of two steels showing opposite behaviors. For the steel in which bainite formation was accelerated by increasing the austenite grain size, the lengthening of sheaves was faster than their nucleation at the grain boundaries, which is consistent with a high  $\Delta Q$ . Conversely, for the steel in which bainite formation was accelerated by decreasing the austenite grain size, nucleation at the grain boundaries was faster than the growth of sheaves, consistent with a small  $\Delta Q$ . It is important then to discuss which aspects of the steel influence  $\Delta Q$  and  $u_T$ .

From Eq. (26), the difference between  $Q_{GB}$  and  $Q_A$  can be understood in terms of different interfacial energies,  $\sigma$ , and different strain energies,  $E_{str}$ . While autocatalytic nucleation takes place at the  $\alpha/\gamma$  interface, grain boundary nucleation takes place at a  $\gamma/\gamma$  interface, and hence they are expected to have different  $\sigma$  values for nucleation.

The strain energy caused by bainite formation can be decreased by self-accommodating variant pairing [61]. Hence, sub-units nucleated by autocatalysis might face a smaller strain energy barrier than the first sub-units formed at the austenite grain boundaries. This effect is of course expected to be less important at larger undercoolings, when the driving force for nucleation is much higher than the strain energy. Table 1 indeed shows that for Steel B  $\Delta Q$  decreases with decreasing temperature, going from 16 kJ mol<sup>-1</sup> at 480 °C to 2 kJ mol<sup>-1</sup> at 370 °C. This effect is not seen in Steel A, which shows a small  $\Delta Q$  of 1 kJ mol<sup>-1</sup> on average throughout the whole reported temperature range.

The first bainite model to distinguish the activation energy by nucleation site is that of Ravi et al. Previous models have used instead an autocatalytic factor ( $\lambda$ ) [20,28,48], which depends on, among other terms,  $\Delta Q$ , as shows Eq. (23). A higher  $\Delta Q$  translates to a higher  $\lambda$ . Rees and Bhadeshia [28] argued that the temporarily higher carbon concentration at the tip of bainite sub-units hinders autocatalysis, and hence proposed that the autocatalytic factor,  $\lambda$ , decreases linearly with the carbon content of the steel. In terms of the present model, this reasoning means a lower  $\Delta Q$  as the carbon content increases.

Indeed, from analyzing the data for steel A-D, higher temperatures and lower carbon content seem to result in a higher  $\Delta Q$ . The effect of

carbon on  $\Delta Q$  is also consistent with the work of Matsuzaki and Bhadeshia [9], in which the low carbon steel analyzed showed an acceleration of bainite formation by increasing the prior austenite grain size, and the high carbon steel showed the opposite behavior.

The reasoning above cannot explain, however, all experimental observations. There are reported cases of low carbon steel in which refining the prior austenite grain size accelerates bainite formation [10], and reported cases of high carbon steel in which refining the grain size decelerates the reaction [3,17].

Alloying elements that segregate to austenite grain boundaries may also influence  $\Delta Q$ . This segregation can change the austenite grain boundary energy and locally change the driving force for bainite nucleation, thus affecting  $Q_{GB}$ . Such an effect was observed by Douguet et al [62], by studying the addition of boron, a chemical element known for segregating to austenite grain boundaries [63]. In the boron-free version of the steel they analyzed, changing the prior austenite grain size had little impact on bainite formation kinetics. When 30 ppm of boron was added, larger prior austenite grains led to faster bainite formation kinetics, indicating that adding boron increased  $\Delta Q$ .

Another aspect that defines the steel's behavior is how the size of the bainite sub-unit varies with changes in the prior austenite grain size. In martensite formation, larger austenite grains result in larger martensite plates. Consequently, increasing the prior austenite grain size accelerates the rate of isothermal martensite formation [64]. The relation between austenite grain size and size of the bainite plates, however, is not straightforward.

Since the sub-unit thickness is mainly controlled by the austenite yield strength [65], it could be expected that a smaller austenite grain size leads to finer sub-units. Note that, considering a fixed aspect ratio, a larger thickness ( $u_T$ ) implies a greater volume ( $V_b$ ). In van Bohemen's model for calculating the bainite plate thickness [34], the Hall-Petch effect is included when calculating the austenite yield strength, and thus the model predicts that smaller austenite grains result in finer bainite plates. This behavior has been verified experimentally for several steels, such as Steel C in the present work [16] and in the data used by van Bohemen in the model optimization.

However, the opposite effect has also been reported, in which a larger prior austenite grain size has led to the formation of finer bainite plates [66,67]. The reason for this behavior is not well explained by the currently available models, which consider  $u_T$  to be a function of austenite strength, driving force for bainite formation, and temperature. Nonetheless, it has already been shown that these three are not the only factor that define the bainite plate thickness, and that dynamic, localized factors such as the creation of dislocations at the bainite/austenite interface and the inhomogeneous distribution of carbon could play a role [65].

Although the bainite model from the present work was able to replicate the effect of the prior austenite grain size on the bainite formation kinetics, its ability to quantitatively predict the effect for a given steel composition and temperature might be limited. If an experimental curve of bainite formation at a given austenite grain size is available, the curve can be fitted to the model and the calculated  $\Delta Q$  can qualitatively point to which behavior the steel might follow (see Fig. 3). For a more accurate prediction, it would be necessary to know beforehand how the size of the bainite sub-unit for the given steel changes with the prior austenite grain size – which is a short-coming of the currently available models for calculating  $u_T$ . Given the limited availability of data in the literature in which both the bainite formation curve and the size of the bainite sub-unit are reported, it was not possible to assess the predictive abilities of the model after extracting  $\Delta Q$  for a given steel composition and temperature from a single curve.

The predictive abilities of the model can be improved by the atomic scale investigation of grain boundary and autocatalytic nucleation. The segregation of elements to austenite grain boundaries can influence  $Q_{GB}$  by locally changing the driving force for bainite nucleation and the boundary's interface energy. Similarly, the buildup of carbon at the tip



of bainite sub-units influences  $Q_A$  by locally decreasing the driving force for bainite nucleation. Understanding such effects can give a better insight into the factors controlling  $\Delta Q$  and how it varies with temperature and chemical composition.

Another important factor that needs to be better understood is how the prior austenite grain size influences the size of the bainite sub-unit. Currently there is no single theory capable of explaining the opposing trends reported in the literature.

## 5. Conclusion

In the present work we developed a model that is capable of replicating both the acceleration and deceleration of the bainite formation kinetics by the refinement of the prior austenite grain size. The proposed model closely matched experimental curves of bainite formation both for steels that showed acceleration and steels that showed deceleration of bainite formation by austenite grain refinement. Two factors were found to define the effect of the prior austenite grain size on the bainite kinetics:

- (i) The difference in the activation energies for grain boundary and autocatalytic nucleation,  $\Delta Q$ . The larger the  $\Delta Q$ , the faster the autocatalytic nucleation in comparison to grain-boundary nucleation, and the more the bainite formation tends to be accelerated by grain coarsening. Low carbon content and low undercooling seem to increase  $\Delta Q$ .
- (ii) The correlation between the thickness of the bainite sub-unit,  $u_T$ , and the prior austenite grain size,  $d_y$ . If  $u_T$  increases with increasing  $d_y$ , bainite formation tends to be faster for larger prior austenite grain sizes. The factors that define the correlation between  $u_T$  and  $d_y$  are not yet clear.

In addition, we also analyzed the input and output parameters of bainite formation models. Most importantly, we have shown that most of the models published in the literature have underestimated the density of initially present potential nucleation sites, resulting in an underestimation of the activation energies for bainite nucleation and overestimation of the lengthening rate of bainite sheaves.

## Code availability

The code necessary to reproduce the findings can be found at <https://github.com/DanielDosSantosAvila/bainite-model>.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.actamat.2024.119656](https://doi.org/10.1016/j.actamat.2024.119656).

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