



Article Mathematical Modelling of Isothermal Decomposition of Austenite in Steel

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Abstract: The main goal of this paper is mathematical modelling and computer simulation of isothermal decomposition of austenite in steel. Mathematical modelling and computer simulation of isothermal decomposition of austenite nowadays is becoming an indispensable tool for the prediction of isothermal heat treatment results of steel. Besides that, the prediction of isothermal decomposition of austenite, optimization and control of microstructure composition and mechanical properties of steel. Isothermal decomposition of austenite is physically one of the most complex engineering processes. In this paper, methods for setting the kinetic expressions for prediction of isothermal decomposition of austenite into ferrite, pearlite or bainite were proposed. After that, based on the chemical composition of hypoeutectoid steels, the quantification of the parameters involved in kinetic expressions was performed. The established kinetic equations were applied in the prediction of microstructure composition of hypoeutectoid steels.

Keywords: mathematical modelling; computer simulation; austenite decomposition kinetics; microstructure transformations

1. Introduction

The research of the mathematical simulation of microstructure distribution in steel is one of the highest-priority research areas in the simulation of phenomena of the heat treatment of steel. By using the additivity rule and kinetic equations of isothermal decomposition of austenite, it is possible to calculate kinetics of austenite decomposition at continuous cooling of steel. The prediction of isothermal decomposition of austenite can be applied for understanding, optimization and control of microstructure composition and mechanical properties of steel [1–4].

The most common method of computer prediction of isothermal decomposition of austenite results is based on the chemical composition of steel by using time-temperature-transformation (TTT) diagrams [5].

Studies of the kinetics of isothermal decomposition of austenite have been intensified in the course of some pioneering studies on the isothermal decomposition of austenite [6–8].

The prediction of microstructure composition is usually based on semi-empirical methods derived from kinetic equations of microstructure transformation [9]. To describe the transformation kinetics by mathematical methods, a semi-empirical approach is employed using the Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation together with additivity rule [10,11].

The phase transformations can be categorized into two categories: reconstructive phase transformations and displacive phase transformations. Decompositions of austenite into ferrite and pearlite in steels are typical examples of reconstructive phase transformations, while martensite, bainite, and Widmanstatten ferrite phase transformations can be recognized as displacive phase transformations [12].



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The formation of ferrite occurs by nucleation at the austenite grain boundaries. After that the ferrite grows inside the austenite grains. The rate of volume fraction of the ferrite is a function of the nucleation rate and the velocity of the ferrite/austenite interface. The nucleation rate is primarily a function of the undercooling below the A_{e3} temperature and the grain size of austenite [13,14].

The nucleation mechanism of pearlite involves the formation of two phases, ferrite and cementite. The nucleation of cementite is a rate-limiting step in hypoeutectoid steels. The proeutectoid ferrite nucleates first and continues to grow with the same crystallographic orientation during the pearlite formation. For hypereutectoid steels, the role of the nucleation of ferrite is a limited process in comparison with the roles of the cementite nucleation. In eutectoid steel, the pearlite nucleation is assumed to occur at the austenite grain corners, edges, and boundaries.

Two different theories are proposed for the growth of pearlite. The Zener–Hillert theory assumes that the volume diffusion of carbon in the austenite is the rate-controlling mechanism [15,16]. In addition, Hillert theory assumes that grain boundary diffusion of the carbon atoms is the rate-controlling mechanism. The nucleation rate of pearlite follows the general nucleation theory [16].

The Johnson–Mehl–Avrami–Kolmogorov (JMAK) theory predicts the overall transformation rate on the basis of nucleation and growth rates. It is the most widely used model to describe the austenite–pearlite transformation kinetics [15].

Bainite was discovered nearly eight decades ago [17]. The research work carried out in the field of bainite is immense [17–20]. A qualitative theory to explain bainite formation still remains a subject of controversy [18,21]. One theory suggests a diffusion-controlled transformation where bainitic growth occurs by a diffusional ledge mechanism, while the other suggests that the bainite reaction is a displacive transformation [18]. Both theories have assumed models to predict the transformation kinetics [22,23]. The growth of bainite and Widmanstatten ferrite requires the partitioning of interstitial carbon. Because of this reason, their growth is controlled by diffusion of interstitial atoms of carbon [12].

Computer simulation of isothermal decomposition of austenite in steel is still a complex problem. The dependence of the physical quantities involved in the kinetic expressions of austenite decomposition has not yet been sufficiently defined in the literature. Efforts are being made to predict the dependence of physical quantities in the kinetic expressions of austenite decomposition on chemical composition.

This work proposes inversion methods for quantification of kinetic parameters and setting the kinetic expressions in the prediction of isothermal decomposition of austenite into ferrite, pearlite, or bainite.

The proposed method of setting kinetic relations can be used in the calculation of characteristic kinetic parameters for other groups of steel. The established model can be used for computer simulation of austenite decomposition in other steels with similar chemical compositions.

2. Materials and Methods

2.1. Methods for Estimation of Kinetic Parameters of Austenite Isothermal Decomposition

2.1.1. Kinetics Expressions of Austenite Decomposition in an Incremental Form

Kinetics of isothermal decomposition of austenite can be defined by Avrami's isothermal equation:

$$K = 1 - \exp(-kt^n) \tag{1}$$

where *X* is transformed part of the microstructure, *t* is time, and *k* and *n* are kinetic parameters. By extracting the time component, Equation (1) can be written as:

$$t = \frac{1}{k^{\frac{1}{n}}} \left(\ln\left(\frac{1}{1-X}\right) \right)^{\frac{1}{n}}$$
(2)

In computer-based mathematical analysis, it is convenient to define the kinetics of austenite decomposition in an incremental form. By differentiating Avrami's equation, it follows that:

$$\frac{dX}{dt} = \exp(-kt^n)nkt^{n-1} \tag{3}$$

After introducing Equation (2) in Equation (3) and a short rearrangement, it follows that:

$$\frac{dX}{dt} = nk^{\frac{1}{n}} \left(\ln \frac{1}{1-X} \right)^{1-\frac{1}{n}} (1-X)$$
(4)

Equation (4) can be written in an incremental form, and the volume fraction $\Delta X^{(N)}$ of austenite transformed in the time interval $\Delta t^{(N)}$ can be calculated as [3]:

$$\Delta X^{(N)} = nk^{\frac{1}{n}} \left(\ln \frac{1}{1 - X^{(N-1)}} \right)^{1 - \frac{1}{n}} \left(1 - X^{(N-1)} \right) \Delta t^{(N)}$$
(5)

where $X^{(N-1)}$ is the volume fraction of austenite transformed in previous N - 1 time intervals. Kinetic parameters *k* and *n* can be evaluated inversely by using data of time of isothermal transformation. The total volume fraction of austenite transformed during isothermal decomposition can be calculated as:

$$X = \sum_{i=1}^{N} \Delta X^{(N)} \tag{6}$$

2.1.2. Ferrite Transformation

The ferrite transformation takes place by the mechanism of nucleation and growth, with the following assumed kinetic parameters [13]:

$$n_{\rm F} = 4 \tag{7}$$

$$k_{\rm F} = \frac{\pi}{3} I_{\rm F} S G_{\rm F}^{\ 3} \tag{8}$$

where *S* is the surface of austenite grain suitable for nucleation, while I_F is the nucleation rate and G_F is the growth rate defined as:

$$I_{\rm F} = T^{-\frac{1}{2}} D_0 \exp\left(-\frac{Q_{\rm dif}}{RT}\right) \exp\left(-\frac{k_1}{RT(\Delta T)^2}\right) \tag{9}$$

$$G_{\rm F} = \frac{c_{\gamma} - c_0}{c_{\gamma} - c_{\alpha}} D_0 \exp\left(-\frac{Q_{\rm dif}}{RT}\right) \frac{1}{y^D}$$
(10)

In Equations (9) and (10), *T* is temperature, ΔT is the undercooling below the critical temperature A_{e3} , D_0 is the material constant, *R* is the universal gas constant, Q_{dif} is the diffusion activation energy, while c_0 , c_{α} , and c_{γ} are the concentrations of steel, ferrite and austenite at the boundary with ferrite, respectively. The effective diffusion length is defined as [7,13]:

$$y^{\mathrm{D}} = \frac{k_2}{\left(\Delta T\right)^{n_1}} \tag{11}$$

where k_1 , k_2 and n_1 are the kinetic parameters dependent on chemical composition of steel. After introducing Equations (9)–(11) in Equation (8), and after some modification, Equation (8) can be rewritten as [14]:

$$k_{\rm F} = SD_0^4 \exp\left(\frac{-4Q_{\rm dif}}{RT}\right) \exp\left(\frac{-k_1}{RT(A_{\rm e3} - T)^2}\right) \left(\frac{c_{\gamma} - c_0}{c_{\gamma} - c_{\alpha}}\right)^3 \left(\frac{(A_{\rm e3} - T)^{n_1}}{k_2}\right)^3 \tag{12}$$

To determine the values of the constants k_1 , k_2 and n_1 , it is first necessary to determine the value of the coefficient k_F for three temperatures, and then to solve a system of three equations with three unknowns (k_1 , k_2 , n_1).

It was assumed that the ferrite transformation does not take place to the end, but to the maximum volume $V_{\text{max}} = V_{\text{rF}} \times V$, when the normalized volume fraction of ferrite can be defined as [18]:

$$\xi_{\rm F} = \frac{X_{\rm F}}{V_{\rm rF}} \tag{13}$$

In Equation (13), X_F is the volume fraction of ferrite and V_{rF} is the relative volume of ferrite. The linear temperature dependence of the volume V_{rF} can be evaluated using an Fe-Fe₃C diagram with the following assumptions: at temperatures A_{e3} and B_s , the volume V_{rF} is equal to 0, while at temperature A_{e1} , it takes the maximum value $V_{rF} = c_0/0.8$ (Figure 1).

 $V_{\rm rF} = a_1 + a_2 T$, for $Ae_3 > T \ge Ae_1$ (14)

where:

$$a_1 = \frac{A_{\rm e3}}{A_{\rm e3} - A_{\rm e1}} \frac{c_0}{0.8} \tag{15}$$

$$a_2 = \frac{-1}{A_{\rm e3} - A_{\rm e1}} \frac{c_0}{0.8} \tag{16}$$

$$V_{\rm rF} = a_3 + a_4 T$$
, for $Ae_1 > T \ge T_F$ (17)

where:

$$a_3 = \frac{-T_{\rm F}}{A_{\rm e1} - T_{\rm F}} \frac{c_0}{0.8} \tag{18}$$

$$a_4 = \frac{1}{A_{\rm e1} - T_{\rm F}} \frac{c_0}{0.8} \tag{19}$$



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Figure 1. Effect of transformation temperature on the volume fraction of proeutectoid ferrite. (a) Scheme of an extension of the eutectoid field with a temperature of austenite decomposition in a Fe-C system; (b) scheme of a TTT diagram for hypoeutectoid steel.

The real volume of ferrite can be written as:

$$dV_{\rm F} = \left(\frac{V_{\rm max} - V_{\rm F}}{V_{\rm max}}\right) dV_{\rm Fe} = \left(\frac{V_{\rm rF}V - V_{\rm F}}{V_{\rm rF}V}\right) dV_{\rm Fe}$$
(20)

$$dV_{\rm F} = (1 - \xi_{\rm F})dV_{\rm Fe} \tag{21}$$

The extended volume of ferrite is defined as:

$$dV_{\rm Fe} = \frac{4}{3}\pi I_{\rm F} S G_{\rm F}^{3} V (t - t_{\rm i})^{3} dt$$
(22)

where t_i is the incubation time. After introducing Equation (22) in Equation (21), it follows that:

$$V_{\rm rF} \, \mathrm{d}\xi_{\rm F} = (1 - \xi_{\rm F}) \frac{4}{3} \pi I_{\rm F} S G_{\rm F}{}^3 (t - t_{\rm i})^3 \mathrm{d}t \tag{23}$$

$$V_{\rm rF} \, \mathrm{d}\xi_{\rm F} = (1 - \xi_{\rm F}) 4k_{\rm F} (t - t_{\rm i})^3 \mathrm{d}t \tag{24}$$

$$V_{\rm rF} \, \frac{{\rm d}\xi_{\rm F}}{(1-\xi_{\rm F})} = 4k_{\rm F}(t-t_{\rm i})^3 {\rm d}t \tag{25}$$

After integrating Equation (25), it follows that:

$$-\ln(1-\xi_{\rm F})V_{\rm rF} = k_{\rm F}t^4 \tag{26}$$

For small values of the normalized volume fraction of ferrite, Equation (26) can be written as:

$$-\ln(1 - X_{\rm F}) = k_{\rm F} t_{\rm i}^4 \tag{27}$$

At any temperature, knowing an incubation time of ferrite transformation, found out from the IT diagram, the value of the kinetic parameter k_F can be written as:

$$k_{\rm F} = \frac{-\ln(1 - X_{\rm Ft_i})}{(t_i)^4} = \frac{-\ln(1 - 0.01)}{(t_i)^4}$$
(28)

From Equation (26), follows the normalized volume fraction of ferrite which is:

$$\xi_{\rm F} = 1 - \exp\left(-\frac{k_{\rm F}}{V_{\rm rF}}t^4\right) \tag{29}$$

Equation (29) can be written in an incremental form, when the normalized volume fraction of ferrite formed by the mechanism of nucleation and growth in the time interval $\Delta t^{(N)}$ can be calculated as:

$$\Delta \xi_{\rm F}^{(\rm N)} = 4 \left(\frac{k_{\rm F}}{V_{\rm rF}}\right)^{\frac{1}{4}} \left(\ln\frac{1}{1-\xi_{\rm F}^{(\rm N-1)}}\right)^{\frac{3}{4}} \left(1-\xi_{\rm F}^{(\rm N-1)}\right) \Delta t^{(\rm N)}$$
(30)

At any time of transformation, the real volume fraction of ferrite can be calculated as $X_F = \xi_F V_{rF}$ (Equation (13)).

2.1.3. Bainite Transformation

The bainite transformation begins at a temperature B_s . Like ferrite transformation, it does not take place to the end, but to the maximum volume $V_{\text{max}} = V_{\text{rB}} \times V$, when the normalized volume fraction of bainite can be defined as [18]:

$$\xi_{\rm B} = \frac{X_{\rm B}}{V_{\rm rB}} \tag{31}$$

where V_{rB} is the relative volume of bainite, while X_B is the volume fraction of bainite defined as:

$$d\xi_{\rm B}V_{\rm rB} = (1 - \xi_{\rm B})I_{\rm B}udt \tag{32}$$

where *u* is the volume of the structural unit of bainite. The nucleation rate is defined as [14]:

$$I_{\rm B} = T^{-\frac{1}{2}} D_0 \exp\left(-\frac{Q_{\rm dif} + k_6}{RT}\right) \exp\left(-\frac{k_7}{RT(\Delta T)^2}\right) \exp\left(-\frac{t_{\rm i}}{t}\right)$$
(33)

where k_6 and k_7 are the kinetic parameters dependent on chemical composition of steel. After introducing Equation (33) to Equation (32), it follows that:

$$\frac{\mathrm{d}\xi_{\mathrm{B}}\Delta V_{\mathrm{rB}}}{(1-\xi_{\mathrm{B}})} = T^{-\frac{1}{2}}D_{0}\exp\left(-\frac{Q_{\mathrm{dif}}+k_{6}}{RT}\right)\exp\left(-\frac{k_{7}}{RT(\Delta T)^{2}}\right)\exp\left(-\frac{t_{\mathrm{i}}}{t}\right)u\mathrm{d}t\tag{34}$$

$$V_{\rm rB} \int \frac{\mathrm{d}\xi_{\rm B}}{(1-\xi_{\rm B})} = T^{-\frac{1}{2}} D_0 \exp\left(-\frac{Q_{\rm dif}+k_6}{RT}\right) \exp\left(-\frac{k_7}{RT(\Delta T)^2}\right) u \int \exp\left(-\frac{t_{\rm i}}{t}\right) \mathrm{d}t \tag{35}$$

If the following is accepted [24]:

$$\int_{0}^{t} \exp\left(-\frac{t_{\rm i}}{t}\right) dt \approx kt^{n} \tag{36}$$

Equation (36) can be rewritten as:

$$-\ln(1-\xi_{\rm B})V_{\rm rB} = T^{-\frac{1}{2}}D_0 \exp\left(-\frac{Q_{\rm dif}+k_6}{RT}\right)\exp\left(-\frac{k_7}{RT(\Delta T)^2}\right)k_8 t^{n_{\rm B}}$$
(37)

where k_8 is the kinetic parameters. The time of bainite transformation can be expressed by:

$$t = \left[\frac{-\ln(1-\xi_{\rm B})V_{\rm rB}}{T^{-\frac{1}{2}}D_0\exp\left(-\frac{Q_{\rm dif}+k_6}{RT}\right)\exp\left(-\frac{k_7}{RT(\Delta T)^2}\right)k_8}\right]^{\frac{1}{n_{\rm B}}}$$
(38)

For small values of the normalized volume fraction of bainite it can be taken that $\ln(1 - \xi_B)V_{rB} \approx \ln(1 - X_B)$; therefore, Equation (38) can be rewritten as:

$$t = \left[\frac{-\ln(1 - X_{\rm B})}{T^{-\frac{1}{2}}D_0 \exp\left(-\frac{Q_{\rm dif} + k_6}{RT}\right) \exp\left(-\frac{k_7}{RT(\Delta T)^2}\right)k_8}\right]^{\frac{1}{n_{\rm B}}}$$
(39)

As a rule, at low temperatures austenite is completely transformed into bainite, when it can be assumed that $V_{rB} \approx 1$ and $\xi_B \approx X_{B}$. With this assumption, the kinetic parameter n_B can be defined as:

$$n_{\rm B} \approx \frac{2.661}{\log(t_{0.99}) - \log(t_{\rm i})}$$
(40)

where t_i is the incubation time and $t_{0.99}$ is the finish time of the isothermal bainite transformation found out from the IT diagram. The denominator of Equation (39) is a function of temperature; therefore, for the incubation time and constant temperature, Equation (39) can be rewritten as:

$$t_{\rm i} = t_{0.01} = \left[\frac{-\ln(1 - X_{\rm B})}{k_{\rm B}}\right]^{\frac{1}{n_{\rm B}}}$$
(41)

At any temperature, knowing an incubation time of bainite transformation, found out from the IT diagram, the value of the kinetic parameter $k_{\rm B}$ can be expressed by:

$$k_{\rm B} = \frac{-\ln(1 - X_{\rm Bt_i})}{(t_i)^{n_{\rm B}}} = \frac{-\ln(1 - 0.01)}{(t_i)^{n_{\rm B}}}$$
(42)

For 99% of austenite transformed into bainite, Equation (38) can be written as:

$$t_{0.99} = \left[\frac{-\ln(1-\xi_{\rm B})V_{\rm rB}}{k_{\rm B}}\right]^{\frac{1}{n_{\rm B}}} = \left[\frac{-\ln\left(1-\frac{X_{\rm B}}{V_{\rm rB}}\right)V_{\rm rB}}{k_{\rm B}}\right]^{\frac{1}{n_{\rm B}}}$$
(43)

where the linear temperature dependence of the volume $V_{\rm rB}$ is assumed:

$$V_{\rm rB} = a_5 + a_6 T.$$
 (44)

Coefficients a_5 and a_6 can be determined by corresponding values of the volume V_{rB} on two different temperatures in IT diagram. Based on Equations (39) and (41), the kinetic parameter k_B can be written as:

$$k_{\rm B} = T^{-\frac{1}{2}} D_0 \exp\left(-\frac{Q_{\rm dif} + k_6}{RT}\right) \exp\left(-\frac{k_7}{RT(\Delta T)^2}\right) k_8 \tag{45}$$

With the previously determined kinetic parameter $n_{\rm B}$, the defined temperature dependence of the volume $V_{\rm rB}$ and with the known values of the constants k_6 , k_7 and k_8 , the kinetics of the bainite transformation is completely defined. To determine the values of the constants k_6 , k_7 and k_8 , it is first necessary to determine the value of the coefficient $k_{\rm B}$ for three temperatures, and then to solve a system of three equations with three unknowns.

Based on Equations (46) and (47), the volume fraction of bainite and the normalized volume fraction of bainite can be determined by:

$$X_{\rm B} = V_{\rm rB} \left(1 - \exp\left(-\frac{k_{\rm B}}{V_{\rm rB}} t^{n_{\rm B}}\right) \right) \tag{46}$$

$$\xi_{\rm B} = \frac{X_{\rm B}}{V_{\rm rB}} = 1 - \exp\left(-\frac{k_{\rm B}}{V_{\rm rB}}t^{n_{\rm B}}\right) \tag{47}$$

Equation (47) can be written in an incremental form, when the normalized volume fraction of bainite formed in the time interval $\Delta t^{(N)}$ can be calculated as:

$$\Delta \xi_{\rm B}^{(\rm N)} = n_{\rm B} \left(\frac{k_{\rm B}}{V_{\rm rB}}\right)^{\frac{1}{n_{\rm B}}} \left(\ln \frac{1}{1 - \xi_{\rm B}^{(\rm N-1)}}\right)^{1 - \frac{1}{n_{\rm B}}} \left(1 - \xi_{\rm B}^{(\rm N-1)}\right) \Delta t^{(\rm N)} \tag{48}$$

At any time of transformation, the real volume fraction of bainite can be calculated as $X_B = \xi_B V_{rB}$ (Equation (31)).

2.1.4. Pearlite Transformation

In the remaining undercooled austenite that has not transformed into ferrite or bainite, at temperatures lower than A_{e1} , the pearlite transformation takes place. The kinetics of pearlite transformation is independent of the kinetics of the previous ferrite or bainite transformation. At temperatures $A_{e1} > T \ge B_s$ the remaining volume available for pearlitic transformation is $V_{rP1} \cdot V$, while at temperatures $T < B_s$ the remaining volume is $V_{rP2} \times V$, where $V_{rP1} = 1 - V_{rF}$ and $V_{rP2} = 1 - V_{rB}$.

For pearlite transformation by the mechanism of nucleation and growth, the following kinetic parameters are assumed:

$$n_{\rm P} = 4 \tag{49}$$

$$k_{\rm P} = \frac{\pi}{3} I_{\rm P} S G_{\rm P}{}^3 \tag{50}$$

where *S* is surface of austenite grain suitable for nucleation, while I_P is the nucleation rate and G_P is the growth rate defined as [14]:

$$I_{\rm P} = T^{-\frac{1}{2}} D_0 \exp\left(-\frac{Q_{\rm dif}}{RT}\right) \exp\left(-\frac{k_3}{RT(\Delta T)^2}\right)$$
(51)

$$G_{\rm P} = \Delta T D_0 \exp\left(-\frac{Q_{\rm dif}}{RT}\right) (c_{\gamma\alpha} - c_{\gamma \rm Fe3C})$$
(52)

In Equations (51) and (52), ΔT is the undercooling below the critical temperature A_{e3} , while $c_{\gamma\alpha}$ and $c_{\gamma Fe3C}$ are the concentrations of austenite at the boundary with ferrite and cementite, respectively. k_3 is the kinetic parameters dependent on chemical composition. After introducing Equations (51) and (52) into Equation (50) and after some modifications, it can be rewritten:

$$k_{\rm P} = SD_0^4 \exp\left(\frac{-4(Q_{\rm dif} + k_5)}{RT}\right) \exp\left(\frac{-k_3}{RT(A_{\rm e1} - T)^2}\right) (c_{\gamma\alpha} - c_{\gamma\rm Fe3C})^3 (A_{\rm e1} - T)^3 k_4^{-4}$$
(53)

To determine the values of the constants k_3 , k_4 and k_5 , it is first necessary to determine the value of the coefficient k_P for three temperatures, and then to solve a system of three equations with three unknowns.

The real volume of pearlite can be written as:

$$dV_{\rm P} = (1 - \xi_{\rm P})dV_{\rm Pe} \tag{54}$$

where the normalized volume fraction can be expressed by:

$$\xi_{\rm P} = \frac{X_{\rm P}}{V_{\rm rP1}} \tag{55}$$

The extended volume of pearlite is defined as:

$$dV_{\rm Pe} = \frac{4}{3}\pi I_{\rm P} S G_{\rm P}{}^3 V (t - t_{\rm i})^3 dt$$
(56)

After introducing Equation (56) into Equation (55), it follows that:

$$V_{\rm rP1} \, \mathrm{d}\xi_{\rm P} = (1 - \xi_{\rm P}) \frac{4}{3} \pi I_{\rm P} S G_{\rm P}{}^3 (t - t_{\rm i})^3 \mathrm{d}t \tag{57}$$

$$V_{\rm rP1} \, \mathrm{d}\xi_{\rm P} = (1 - \xi_{\rm P}) 4k_{\rm P} (t - t_{\rm i})^3 \Delta \mathrm{d}t \tag{58}$$

$$V_{\rm rP1} \, \frac{d\xi_{\rm P}}{(1-\xi_{\rm P})} = 4k_{\rm P}(t-t_{\rm i})^3 dt \tag{59}$$

After integrating Equation (59), it follows that:

$$-\ln(1-\xi_{\rm P})V_{\rm rP1} = k_{\rm P}t^4 \tag{60}$$

For small values of the normalized volume fraction of perlite, Equation (60) can be written as:

$$-\ln(1 - X_{\rm P}) = k_{\rm P} t_{\rm i}^4 \tag{61}$$

At any temperature, knowing the incubation time of pearlite transformation, found out from the IT diagram, the value of the kinetic parameter k_P can be written as:

$$k_{\rm P} = \frac{-\ln(1 - X_{\rm Pt_i})}{(t_i)^4} = \frac{-\ln(1 - 0.01)}{(t_i)^4}$$
(62)

From Equation (60) follows the normalized volume fraction of pearlite, which is:

$$\tilde{\xi}_{\rm P} = 1 - \exp\left(-\frac{k_{\rm P}}{V_{\rm rP1}}t^4\right) \tag{63}$$

As for ferrite and bainite transformation, Equation (63) can be written in an incremental form. The normalized volume fraction of pearlite formed by the mechanism of nucleation and growth in the time interval $\Delta t^{(N)}$ can be calculated by:

$$\Delta \xi_{\rm P}^{\rm (N)} = 4 \left(\frac{k_{\rm P}}{V_{\rm rp1}}\right)^{\frac{1}{4}} \left(\ln \frac{1}{1 - \xi_{\rm P}^{\rm (N-1)}}\right)^{\frac{3}{4}} \left(1 - \xi_{\rm P}^{\rm (N-1)}\right) \Delta t^{\rm (N)} \tag{64}$$

The presented method for estimation of $k_{\rm P}$ and $\xi_{\rm P}$ is also valid at temperatures lower than $B_{\rm s}$. In that case, in the above equations, the relative volume $V_{\rm rP1}$ should be replaced by the relative volume $V_{\rm rP2}$.

2.2. Materials

With the aim of qualitatively and quantitatively defining the influence of chemical composition on the isothermal decomposition of austenite, the values of kinetic parameters were investigated on a number of hypoeutectoid, low-alloy steels [25]. Their composition is shown in Table 1.

Table 1. Chemical composition of studied steels (balance Fe).

Designation	Chemical Composition, wt. %									
(DIN)	С	Si	Mn	Р	S	Cr	Cu	Мо	Ni	V
42CrMo4	0.38	0.23	0.64	0.019	0.013	0.99	0.17	0.16	0.08	< 0.01
Ck45	0.44	0.22	0.66	0.022	0.029	0.15	-	-	-	0.02
28NiCrMo74	0.30	0.24	0.46	0.030	0.025	1.44	0.20	0.37	2.06	< 0.01
34Cr4	0.35	0.23	0.65	0.026	0.013	1.11	0.18	0.05	0.23	< 0.01
25CrMo4	0.22	0.25	0.64	0.010	0.011	0.97	0.16	0.23	0.33	< 0.01
36Cr6	0.36	0.25	0.49	0.021	0.020	1.54	0.16	0.03	0.21	< 0.01
41Cr4	0.44	0.22	0.80	0.030	0.023	1.04	0.17	0.04	0.26	< 0.01

3. Results

Section 2.1 presents methods for estimating kinetic parameters, which completely define the kinetics of austenite isothermal decomposition into ferrite, pearlite and bainite. The calculated values of the kinetic parameters depend on the chemical composition, i.e., they are valid only for one steel.

The critical temperatures of austenite decomposition were calculated based on Equations (65) and (66) [26], and Equation (67) [27].

$$A_{e3} = 883.49 - 275.89\%C + 90.91(\%C)^{2} - 12.26\%Cr + 16.45\%C\%Cr - 29.96\%Mn + 23.50\%C\%Mn + 8.49\%Mo - 10.80\%C\%Mo - 25.56\%Ni + 14.71\%C\%Ni + 1.45\%Mn\%Ni + 0.76(\%Ni)^{2} + 13.53\%Si - 3.47\%Mn\%Si$$
(65)

$$A_{e1} = 727.37 + 13.40\% Cr - 1.03\% C\% Cr - 16.72\% Mn + 0.91\% C\% Mn + 6.18\% Cr\% Mn - 0.64(\% Mn)^{2} + 3.14\% Mo + 1.86\% Cr\% Mo - 0.73\% Mn\% Mo - 13.66\% Ni + 0.53\% C\% Ni + 1.11\% Cr\% Ni - 2.28\% Mn\% Ni - 0.24(\% Ni)^{2} + 6.34\% Si - 8.88\% Cr\% Si - 2.34\% Mn\% Si + 11.98(\% Si)^{2}$$
(66)

$$B_{\rm s} = 830 - 270\% \text{C} - 90\% \text{Mn} - 37\% \text{Ni} - 70\% \text{Cr} - 83\% \text{Mo}$$
(67)

The dependence of kinetic parameters of ferrite, pearlite and bainite transformation on the content of carbon, chromium, molybdenum and nickel was estimated by regression analysis (Equations (68)–(78)). Because of the similar content of manganese and silicon in studied steels, these elements were not included in the regression analysis. Based on the proposed equations, the kinetic parameters involved in mathematical model of ferrite, pearlite and bainite transformation can be calculated for any other chemical composition of hypoeutectoid, low-alloy steels (Table 2).

$$k_2 = \exp(-4.02 - 11.11\% C - 1.99\% Cr + 20.76\% Mo - 40.99\% Ni)$$
(68)

$$n_1 = 6.23 - 2.25\% C - 0.81\% Cr + 5.17\% Mo - 8.83\% Ni$$
 (69)

$$k_3 = 106003024.20 - 51200507.88\% C - 19751485.43\% Cr - 256581910.00\% Mo + 25605277.23\% Ni$$
(70)

$$k_4 = \exp(-33.63 + 61.93\%\text{C} - 15.96\%\text{Cr} + 6.20\%\text{Mo} - 3.60\%\text{Ni})$$
(71)

$$k_5 = 97606.14 - 488262.55\%\text{C} + 134064.43\%\text{Cr} + 28612.33\%\text{Mo} + 29497.32\%\text{Ni}$$
(72)

$$k_6 = 190361.38 - 288009.61\%\text{C} - 76052.87\%\text{Cr} - 693123.59\%\text{Mo} + 78021.58\%\text{Ni}$$
 (73)

$$k_7 = \exp(10.37 + 24.69\%\text{C} + 1.24\%\text{Cr} - 9.98\%\text{Mo} + 2.63\%\text{Ni})$$
(74)

$$k_8 = \exp(81.35 - 73.62\%\text{C} - 16.43\%\text{Cr} - 127.88\%\text{Mo} + 14.57\%\text{Ni})$$
(75)

$$n_{\rm B} = 1.57 + 1.74\% \text{C} - 0.47\% \text{Cr} - 1.79\% \text{Mo} + 0.16\% \text{Ni}$$
 (76)

$$a_5 = -1.0130 + 3.7800\%$$
C + 1.8340%Cr + 4.2012%Mo + 0.4655%Ni (77)

$$a_6 = 0.003525 - 0.006847\% C - 0.002777\% Cr - 0.006653\% Mo - 0.001100\% Ni$$
 (78)

Table 2. Kinetic parameters of austenite isothermal decomposition.

Transformetion	Constant	Steel Designation (DIN)							
Iransformation		42CrMo4	Ck45	28NiCrMo74	34Cr4	25CrMo4	36Cr6	41Cr4	
Ferrite	k_1	$2.5 imes 10^5$	$2.5 imes 10^5$	-	$2.5 imes 10^5$	$2.5 imes 10^5$	$2.5 imes 10^5$	$2.5 imes 10^5$	
	k_2	$3.8321 imes10^{-5}$	1.7441×10^{-4}	-	$9.0625 imes 10^{-10}$	$6.3183 imes10^{-8}$	8.8213×10^{-9}	$1.1941 imes10^{-9}$	
	n_1	4.6923	5.2095	-	2.3955	3.3200	2.5230	2.3547	
	a_1	8.8839	8.7592	-	7.8504	3.1064	10.0511	14.7870	
	<i>a</i> ₂	-0.0115	-0.0114	-	-0.0101	-0.0039	-0.0130	-0.0195	
	<i>a</i> ₃	-1.8688	-4.4695	-	-1.7667	-1.4606	-1.5163	-1.7387	
	a_4	0.0032	0.0070	-	0.0030	0.0024	0.0027	0.0031	
Pearlite	<i>k</i> ₃	27,988,177	76,767,479	16,492,913	31,355,038	43,316,272	56,142,707	93,514,410	
	k_4	$1.1450 imes 10^{-11}$	$9.8057 imes10^{-5}$	$2.1918 imes 10^{-19}$	$6.1325 imes 10^{-12}$	$8.6385 imes 10^{-17}$	$2.5088 imes 10^{-17}$	$5.4094 imes 10^{-12}$	
	k_5	51,728	-92,146	214,273	47,324	149,610	151,595	46,211	
Bainite	k_6	-99,033	51,128	-101,946	-15,089	-77,442	-34,123	-16,704	
	k_7	3.2308×10^{8}	$2.4803 imes10^9$	$2.0943 imes 10^{9}$	$2.5027 imes 10^9$	$2.5966 imes 10^{6}$	2.2482×10^{9}	$1.6819 imes 10^9$	
	k_8	$5.4488 imes 10^7$	$1.1746 imes 10^{20}$	$8.1265 imes 10^7$	$8.0362 imes 10^{14}$	$6.6340 imes 10^{10}$	$2.7482 imes 10^{12}$	4.2311×10^{13}	
	n _B	1.4923	2.30043	1.09856	1.58602	1.12141	1.51777	1.74637	
	<i>a</i> ₅	2.989028	1.000000	-	2.349733	2.794667	3.587317	2.881892	
	<i>a</i> ₆	-0.003041	0.00000	-	-0.002139	-0.002667	-0.003902	-0.002973	

4. Discussion

The values of kinetic parameters given in Table 2 were verified by comparing the modeled curves of the isothermal transformation (IT) diagram of steel 42CrMo4, 36Cr6, Ck45, and 28NiCrMo74 with those obtained experimentally. In Figures 2–5, the dashed lines show the experimental IT diagram, while the mathematically determined times of start (incubation time) and times of finish of the isothermal austenite decomposition, $t_{0.01}$ and $t_{0.99}$, are shown by solid lines. Additionally, Figure 2 shows curves corresponding to bainite volume fraction of 25%, 50%, 75% and 90%.







Figure 3. IT diagram of steel 36Cr6.







Figure 5. IT diagram of steel 28NiCrMo74.

The times of start and finish of isothermal decomposition of austenite were calculated based on Equations (30), (48) and (64), and the known values of the kinetic parameters.

Kinetic parameters of ferrite, bainite and pearlite transformation, k_F , k_B and k_P , were calculated by Equations (12), (45) and (53), respectively. Other physical quantities used in the developed mathematical model are shown in Table 3.

Table 3. Physical quantities used in modelling of austenite isothermal decomposition.

Quantity Value	Units	Description
$D_0 = 2.3 \times 10^{-5}$	$\mathrm{m}^2\mathrm{s}^{-1}$	Material constant
$Q_{\rm dif} = 1.48 \times 10^5$	$J \mathrm{mol}^{-1}$	Diffusion activation energy
<i>R</i> = 8.314	$J \text{ mol}^{-1} \text{ K}^{-1}$	Universal gas constant
<i>S</i> = 170153	m^{-1}	Surface of austenite grain suitable for nucleation
$c_{\gamma} = 1186.661 \exp(-7.2834 \times 10^{-3} T)$	wt.% C	Concentration of austenite
$c_{\alpha} = 0.1592 - 1.3423 \times 10^{-4} T$	wt.% C	Concentration of ferrite
$c_{\gamma \alpha} = 9.6782 - 8.82 \times 10^{-3} T$	wt.% C	Concentration of austenite at the boundary with ferrite
$c_{\gamma \text{Fe3C}} = -0.5248 + 1.28 \times 10^{-3} \ T$	wt.% C	Concentration of austenite at the boundary with cementite

Figures 2–5 show that differences between times of transformations in experimentally and mathematically determined IT diagrams are not relevant. Therefore, it is seen that the kinetic parameters involved in an established mathematical model of ferrite, pearlite and bainite transformation can be successfully determined on the basis of Equations (68)–(78) with high accuracy. Developed model avoids the use of simple empirical expressions in predictions of isothermal decomposition of austenite.

Since the developed model is written in incremental form, it is suitable for predicting austenite decomposition during the continuous cooling of steel using Scheil's additivity rule. Additionally, it is very easy to extend this approach in the prediction of the kinetics of austenite decomposition for other types of steel.

5. Conclusions

In this paper, the equations for the estimation of microstructure constituents' volume fractions after the isothermal decomposition of austenite have been proposed. Isothermal decomposition of austenite implies quenching of steel from the austenite range to the temperature of isothermal transformation where all austenite decomposes at a constant temperature.

The inversion methods for the calculation of characteristic variables in the mathematical model of kinetics of austenite decomposition were developed.

The mathematical model was verified by the comparison of experimentally and mathematically determined IT diagrams of steel. It can be concluded that characteristic parameters included in the mathematical model of ferrite, pearlite and bainite transformation can be successfully evaluated by the proposed method.

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References

- 1. Pan, J.; Gu, J.; Zhang, W. Industrial Applications of Computer Simulation of Heat Treatment and Chemical Heat Treatment. In *Handbook of Thermal Process Modeling of Steels*; Gür, C.H., Pan, J., Eds.; CRC Press: Boca Raton, FL, USA, 2009; pp. 673–701.
- Reti, T.; Felde, I.; Guerrero, M.; Sarmiento, S. Using generalized time-temperature parameters for predicting the hardness change occurring during tempering. In Proceedings of the International Conference on New Challenges in Heat Treatment and Surface Engineering, Dubrovnik–Cavtat, Dubrovnik, Croatia, 9–12 June 2009; Smoljan, B., Matijević, B., Eds.; Listemann AG: Bendern, Switzerland, 2009; pp. 333–342.
- 3. Smokvina Hanza, S. Mathematical Modeling and Computer Simulation of Microstructure Transformations and Mechanical Properties During Steel Quenching. Ph.D. Thesis, University of Rijeka, Rijeka, Croatia, 2011. (In Croatian)
- 4. Smoljan, B.; Iljkić, D.; Totten, G. Mathematical modeling and simulation of hardness of quenched and tempered steel. *Met. Mater. Trans. B* 2015, *46*, 2666–2673. [CrossRef]
- 5. Rose, A.; Wever, F. Atlas zur Wärmebehandlung der Stähle I; Verlag Stahleisen: Düsseldorf, Germany, 1954.
- 6. Hillert, M. Discussion of "a personal commentary on transformation of austenite at constant subcritical temperatures". *Metall. Mater. Trans. A* **2011**, *42*, 541–542. [CrossRef]
- 7. Zener, C. Kinetics of decomposition of austenite. *Trans. AIME* 1946, 167, 550–595.
- 8. Zener, C. Theory of growth of spherical precipitates from solid solution. J. Appl. Phys. 1949, 20, 950–953. [CrossRef]
- 9. Serajzadeh, S. A mathematical model for prediction of austenite phase transformation. Mater. Lett. 2004, 58, 1597–1601. [CrossRef]
- 10. Militzer, M.; Hawbolt, E.B.; Meadowcroft, T.R. Microstructural model for hot strip rolling of high-strength low-alloy steels. *Met. Mater. Trans. A* **2000**, *31*, 1247–1259. [CrossRef]
- 11. Avrami, M. Kinetics of phase change. I general theory. J. Chem. Phys. 1939, 7, 1103–1112. [CrossRef]
- 12. Simsir, C.; Gür, C.H. Simulation of quenching. In *Handbook of Thermal Process Modeling of Steels*; Gür, C.H., Pan, J., Eds.; CRC Press: Boca Raton, FL, USA, 2009; pp. 341–425.
- 13. Christian, J.W. The Theory of Transformations in Metals and Alloys, 1st ed.; Pergamon Press: Oxford, UK, 2002.
- 14. Suehiro, M. A mathematical model for predicting temperature of steel during cooling based on microstructural evolution. In Proceedings of the 11th Congress of IFHTSE and 4th ASM Heat Treatment and Surface Engineering Conference in Europe, Florence, Italy, 19–21 October 1998; Volume 1, pp. 11–20.
- 15. Offerman, S.; van Wilderen, L.; van Dijk, N.; Sietsma, J.; Rekveldt, M.; van der Zwaag, S. In-situ study of pearlite nucleation and growth during isothermal austenite decomposition in nearly eutectoid steel. *Acta Mater.* **2003**, *51*, 3927–3938. [CrossRef]
- 16. Whiting, M. A reappraisal of kinetic data for the growth of pearlite in high purity Fe-C eutectoid alloys. *Scr. Mater.* **2000**, *43*, 969–975. [CrossRef]
- 17. Davenport, E.S.; Bain, E.C. Transformation of austenite at constant subcritical temperatures. *Trans. Met. Soc. AIME* **1930**, *90*, 117–154.
- 18. Bhadeshia, H.K.D.H. *Bainite in Steels: Transformations, Microstructure and Properties,* 2nd ed.; IOM Communications: London, UK, 2001.
- 19. Fielding, L.C.D. The bainite controversy. *Mater. Sci. Technol.* **2013**, *29*, 383–399. [CrossRef]
- 20. Yang, Z.-G.; Fang, H.-S. An overview on bainite formation in steels. Curr. Opin. Solid State Mater. Sci. 2005, 9, 277–286. [CrossRef]
- 21. Hillert, M. The nature of bainite. ISIJ Int. 1995, 35, 1134–1140. [CrossRef]
- 22. Quidort, D.; Bréchet, Y.J.M. A model of isothermal and non isothermal transformation kinetics of bainite in 0.5% C steels. *ISIJ Int.* **2002**, *42*, 1010–1017. [CrossRef]
- 23. Rees, G.I.; Bhadeshia, H.K.D.H. Bainite transformation kinetics part 1 modified model. *Mater. Sci. Technol.* **1992**, *8*, 985–993. [CrossRef]
- 24. Pan, Y.-T. Measurement and Modelling of Diffusional Transformation of Austenite in C.-Mn Steels. Ph.D. Thesis, Institute of Materials Science and Engineering of the National Sun Yat-Sen University, Kaohsiung, Taiwan, 2001.
- 25. Rose, A.; Hougardy, H. Atlas zur Wärmebehandlung der Stähle; Verlag Stahleisen: Düsseldorf, Germany, 1972.
- 26. Lusk, M.T.; Lee, Y.-K. A global material model for simulating the transformation kinetics of low alloy steels. In Proceedings of the 7th International Seminar of IFHT: Heat Treatment and Surface Engineering of Light Alloys, Budapest, Hungary, 15–17 September 1999; Lendvai, J., Réti, T., Eds.; Hungarian Scientific Society of Mechanical Engineering: Budapest, Hungary, 1999; pp. 273–282.
- 27. Steven, W.; Haynes, A.G. The temperature of formation of martensite and bainite in low alloy steels. *J. Iron Steel Inst.* **1956**, *183*, 349–359.