Original Article

Peritectic phase transformation in the Fe–Mn and Fe–C system utilizing simulations with phase-field method

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The present investigation focuses on the solidification of peritectic binary alloys in the systems Fe–Mn and Fe–C by utilizing phase-field simulations. Isothermal and directional solidification conditions were simulated with this approach and the following aspects were investigated: the phases evolution during the peritectic transformation close to the peritectic temperature for the Fe–Mn alloys with 9.5 and 11.0 wt.%, the kinetics of the γ-phase growth simultaneously into the liquid and into the δ-phase during the peritectic transformation for several alloys under isothermal conditions in the Fe–Mn peritectic plateau, the γ-phase thickness during the peritectic reaction in the Fe–Mn system and, finally, the behavior of the remaining δ-phase amount at the end of solidification for different cooling rates in the Fe–C peritectic alloy. The model approach was checked by comparison with literature data. It was concluded that the present approach is consistent in yielding quantitative results for the interested phase transformation.

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1. Introduction

An increase of applications of mathematical modeling and computational modeling to describe important phenomena in metallurgy, materials science and materials engineering can be noticed over the last three decades. Many advances in this direction can be observed and a prominent mathematical method to emulate phase transformations in materials science is the well-known phase-field method (PFM). This method has also been extensively applied to simulations of solidification of metals and alloys [1–9] and to explore different aspects of the solidified structure. Some examples that can be highlighted are the dendrite growth [10], the multi-component solidification [11], the simulation of the columnar-to-equiaxed transition (CET) [12] and the dendrite growth under a fluid flow regime [13].
Although simulations utilizing the PFM for the case of peritectic phase transformation may be found in the literature [14,15], investigations of the fundamental aspects for the case of Fe–Mn system with alloy concentrations in the range of medium manganese steel (MMnS) grades (around 10 wt.% of Mn) are not common. Therefore, this later point motivates the development of the present work, since these steel grades along with the high manganese steel (HMnS) grades (manganese content from 15 to 25 wt.% and aluminum content until 8 wt.%) normally show peritectic phase transformation during the solidification process and are subject of an intensive investigation, especially in experimental works, in Germany and South Korea over approximately a decade. Nevertheless, the most popular peritectic phase transformation in the case of steels is the one in the Fe–C system. Different types of techniques for modeling this phase transformation can be found in the literature [16–18] and this system was also included in the present investigation.

For the case of Fe–Mn system, simulations for binary alloys were carried out and the kinetics of the phases evolution were taken into account. With this purpose, 1-D and 2-D simulations were performed and the mathematical parameters of the traditional power-law function, from the experimental field, that describes the γ-phase thickness evolution with time were determined based on the simulation results. The investigation was conducted for isothermal conditions and for different chemical compositions in the peritectic plateau (hypoperitectic, peritectic and hyperperitectic) to check the behavior of the kinetics. This investigation focuses on the characterization of the kinetics of the second stage of peritectic phase transformation, since this phase transformation takes place in two stages, first the peritectic reaction and afterwards the peritectic transformation – according to the nomenclature proposed by St. John and Hogan [16]. Details of the two stages of the peritectic phase transformation are described by St. John and Hogan [19] and Alves et al. [20].

After performing investigations utilizing isothermal simulations for the Fe–Mn system, simulations of directional solidification were carried out with the numerical model for the same system to examine the growth characteristics of the new solid phase (the γ-phase) on the first solid phase (δ-phase). This growth of the γ-phase on the δ-phase is known as peritectic reaction, or the first stage of peritectic phase transformation. According to Fredriksson and Nylén [18], during the peritectic reaction, the γ-phase thickness close to the triple point would be constant and equal to twice radius of the γ tip. In addition to that, this γ-phase thickness would be influenced by the equilibrium concentrations of the phase diagram and by the interfacial tensions between the phases. Fig. 1 shows a sketch adapted from Ref. [21] to clarify the growth of the γ-phase on the δ-phase during the peritectic reaction. These authors [21] suggested also an analytical theory to estimate the γ-phase thickness during this stage. Therefore, numerical simulations were performed varying the δ–γ interfacial tension and the results for the γ-phase thickness under steady-state growth were utilized for comparison with the analytical theory.

2-D simulations under directional solidification conditions were performed with the numerical model for the Fe–C system with peritectic alloy concentration. These simulations were carried out in order to investigate the behavior of the remaining δ-phase at the end of the solidification for different solidification conditions, i.e., for different cooling rates. A diagram for the percentage of remaining δ-phase versus the cooling rate is presented and a mathematical functional to estimate the remaining amount of the δ-phase as a function of the cooling rate is suggested based on the simulation results.

2. Peritectic phase-field model description

The phase-field model utilized in the present investigation is for the case of binary alloys and corresponds to an adaptation of the numerical model initially proposed by Folch and Plapp [22] for the case of eutectic transformation. This adaptation was able to be done because, similarly to the eutectic phase transformation, the peritectic phase transformation involves the presence of two solid phases with the liquid. Additionally, this approach proposed by these authors is able to reproduce the so-called sharp-interface limit and the thermodynamic equilibrium can be defined by a linearization of the phase diagram (straight liquidus and solidus lines) for the case of binary alloys. The slopes of liquidus and solidus lines are m and to m/k, respectively, where k is the partition coefficient. This way of describing the thermodynamic equilibrium using linearization of the phase diagram is completely acceptable in the present investigation and it promotes a significant gain in the computational time (CPU time).

By following the variational formulation discussed by Folch and Plapp [22] and by utilizing the conversion of dimensional variables in dimensionless variables [2,7,8,22], the differential equation that describes the evolution of phase-field variables, \( p_i \) with \( i = \delta, \gamma, L \), can be expressed by Eq. (2.1).

\[
\begin{align*}
\frac{\partial p_i}{\partial t} &= \delta^2 \frac{\partial}{\partial x} \left[ \frac{2}{3} \left( -2p_i(1-p_i)(1-2p_i) + \sum_{j \neq i} p_j(1-p_j)(1-2p_j) \right) + \\
\left( a_i p_j p_k \left[ p_i + p_j + p_k \right] \right) f_{i,j,k} - 2f_{i,j} \right] + \\
\sum_{j \neq i} \frac{\partial g_j}{\partial p_i} \left|_{\gamma_{i,j},n_{i,j}=1} \right) (\mu_{A_j} - B_j) 
\end{align*}
\]  

(2.1)
where

\[ f_{a,k} = p_i \rho_j + p_k \left( 1 + b \frac{p_j}{3} \right) \]  
\[ f_{b,k} = p_i \rho_j \left( \frac{1}{2} + b \frac{p_j}{3} \right) \]  
\[ \text{If } p_k \neq 1 \]  
\[ r(\bar{p}) = \bar{t} + \frac{r_i - r_k}{2} \left( \frac{p_i - p_k}{p_i + p_k} \right) \]  
\[ \text{If } p_k = 1 \]  
\[ r(\bar{p}) = \bar{t} \]

For isothermal solidification:

\[ A_i(T) = c_i + (k_i - 1) \frac{(T - T_f)}{m_i \Delta T} \]  
\[ B_i(T) = A_i(T) \frac{(T - T_f)}{m_i \Delta T} \]  

For directional solidification simulations:

\[ A_i(T) = c_i + \frac{(k_i - 1)}{m_i} \cdot \frac{|m_i| (\bar{z} - \bar{u}_p \bar{t})}{l_p} \]  
\[ B_i(T) = \frac{A_i(T)}{m_i} \cdot \frac{|m_i| (\bar{z} - \bar{u}_p \bar{t})}{l_p} \]

and

\[ g_i = \frac{P_i^2}{4} \left\{ 15(1 - p_i) \left[ 1 + p_i - (p_k - p_j) \right] + p_i(9p_j^2 - 5) \right\} \]  
\[ \mu = c - \sum_i A_i(T) h_i(\bar{p}) \]

\[ \lambda = \frac{W a_1}{d} \left( \frac{1}{|A_L - A_i|} + \frac{1}{|A_L - A_i|} \right) \]  
\[ c_i = \frac{C_i - C_L}{\Delta C} \]  
\[ l_p = \frac{|m_i| \Delta C}{G} \]  

The description of the mathematical equations can represent the phases \( \delta, \gamma, L \) depending on the context and different indices in the same equation mean different phases. As \( p_i + p_j + p_k = 1 \), the Eq. (2.1) can be solved numerically for only two phases and the third phase is determined by difference.

In addition to the differential equations for the phase-field variables (Eq. (2.1)), it is necessary to solve the composition field numerically for each time-step during the simulation. Nevertheless, according to Eq. (2.9), the dimensionless chemical potential and the concentration field are related to each other and solving one of them already guarantees the solution of the other. Therefore, the differential equation of the dimensionless chemical potential is presented in Eq. (2.13). This later was obtained applying the non-variational formulation proposed and well-discussed in the literature [22]. Eq. (2.13) contemplates also the anti-trapping term normally incorporated in this type of PFM approach.

\[ \frac{\partial \mu}{\partial t} = \nabla \cdot \left[ D_{L_i} \frac{\partial p_i}{\partial T} + D_{\delta} \frac{\partial p_i}{\partial \bar{t}} \right] \left( \bar{v} \mu \right) - \sum_i A_i \frac{\partial p_i}{\partial t} + 2 \cdot a \cdot \sum_{i=\delta,\gamma} (A_i - A_{L_i}) \left( -\frac{\nabla p_i}{\left| \nabla p_i \right|} \cdot \frac{\nabla p_i}{\left| \nabla p_i \right|} \right) \]

(2.13)

The terms \( D_L, D_{\delta} \) and \( D_\gamma \) are the dimensionless diffusion coefficients of liquid, \( \delta \)-phase and \( \gamma \)-phase, \( a \) is a constant equal to \( 1/2\sqrt{\pi} \) and \( A_i = A_i(T) \) is already defined by Eqs. (2.4) and (2.6).

The numerical technique utilized to solve for each time-step the described differential equations was based on the finite-difference method. The state of the simulated domain was calculated based on the previous time-step and after that, the fields of phases and chemical composition were updated for the next time-step. Thus, the evolution of the phase transformation was evaluated.

3. Analytical theory for the peritectic reaction

According to Fredriksson and Nylen [21], the γ-phase thickness during the steady-state growth of the γ-phase on the δ-phase can be estimated analytically by Eqs. (3.1) and (3.2), where: $D_L$ is the liquid diffusion coefficient, $\nu$ is the speed of γ-phase growth, $\Delta G_m$ is the driving force, $\nu_m$ is the molar volume of liquid, and $\sigma_{IL}$, $\sigma_{\gamma L}$, and $\sigma_{\gamma \gamma}$ are the interfacial tensions. Three can notice that the γ-phase thickness proposed by this authors [21], $\nu^\gamma_{\text{phase}}$, depends essentially on the equilibrium concentrations defined by the phase diagram and on the interfacial tensions of the involved phases. The sketches of Figs. 1 and 2 serve to clarify the meaning of the γ-phase thickness during the peritectic reaction and the equilibrium concentrations of the analytical model for a defined undercooling ($\Delta T_{UC}$). Further details can be found in Ref. [21].

$$\nu^\gamma_{\text{phase}} = \frac{0.034 \cdot D_L}{\nu} \left( \frac{X_B^{\delta} - X_B^{\gamma}}{X_B^{\gamma} - X_B^{\beta}} \right)^3 \left( \frac{1}{1 - 2 \cdot \frac{1}{\pi} \left( \frac{X_B^{\gamma} - X_B^{\beta}}{X_B^{\gamma} - X_B^{\beta}} \right)^2 \left( \frac{X_B^{\gamma} - X_B^{\beta}}{X_B^{\gamma} - X_B^{\beta}} \right)} \right)^3$$  \hspace{1cm} (3.1)

$$\nu^\gamma_{\text{phase}} = \nu^\gamma_{\text{phase}} (\sigma_{IL}, \sigma_{\gamma L}, \sigma_{\gamma \gamma}) = \left( \frac{\sigma_{IL} + \sigma_{\gamma L} - \sigma_{\gamma \gamma}}{-\Delta G_m} \right) \cdot \nu_m \hspace{1cm} (3.2)$$

4. Method and materials description

The values of liquidus line slopes for each phase and the partition coefficients were determined based on phase diagrams from Thermo-Calc® [24] (thermodynamic database TCFE7) for both investigated systems. The liquidus line slopes were calculated by linear regression of the phase diagram data and the partition coefficients were determined by averaging ratios of the solid concentration to liquid concentration. The complete data for both explored system can be found in Table 2 for the Fe–Mn system and in Table 3 for the Fe–C system. By utilizing these tables together with the sketch of Fig. 2, it is also possible to determine the phase diagram close to the peritectic temperature. These tables contain also information about the utilized physical data for each system and parameters of the numerical simulations.

The diffusion coefficients were calculated exactly at the peritectic temperature in both analyzed systems. In the Fe–Mn system, the diffusion data of the γ-phase was taken from DICTRA® [25] (thermodynamic database TCFE7, mobility...
database MOB2), for the δ-phase from Ref. [26] and for the liquid from Ref. [27]. In the Fe–C system, the diffusion coefficients for δ-phase, γ-phase and liquid were taken from Ref. [27].

The dimensionless grid spacing, \( \Delta x \), of the numerical simulations was set equal to 0.8 and the dimensionless time increment, \( \Delta t \), has followed the values found in the literature [22].

The first investigations were carried out in 1-D, under isothermal conditions with an undercooling (\( T_p - T \)) equal to 1 K and for different concentrations in the peritectic plateau of the Fe–Mn system. Hypoperitectic, peritectic and hyperperitectic alloys were investigated with this pattern. The numerical domain dimension for these simulations was equal to 162 μm. This size of domain is in the range of secondary dendrite arm spacing for steels [28] and it was defined assuming the fact that the second solid phase arise normally between the secondary dendrite arms of first solid phase in peritectic phase transformation. In the beginning of each simulation, the phase fractions of δ-phase and liquid inside the numerical domain have respected the lever rule at peritectic temperature. Before starting the simulations, a small nucleus of γ-phase was positioned on the δ-liquid interface. The simulations of hypoperitectic and peritectic alloys were performed until the total amount of solid became higher than 99.7% and the simulations of hyperperitectic alloys until the percentage of δ-phase became lower than 0.3%, since the γ-phase and the liquid are expected in the final stage of phase transformation for the latter cases. This approach allows simulating the peritectic transformation, the second stage of the peritectic phase transformation, since the simulations were in 1-D and there is no occurrence of the triple-point. This 1-D simulation can be comparable to a simulation of radial growth with restriction of diffusion only on radial direction.

Based on the approach presented in the last paragraph, the evolution of the phases was quantitatively defined and the evolution of γ-phase thickness with time was determined for all simulations. The mathematical coefficient \( A \) and the exponent \( n \) of the power-law (Eq. (4.1)) were determined for each simulation utilizing the linear regression of the natural logarithm of the γ-phase thickness versus the natural logarithm of the simulation time. This mathematical equation is the proposed equation found in the experimental literature [29–31] to describe quantitatively the growth kinetics of the γ-phase thickness during the peritectic phase transformation under solidification conditions close to the thermodynamic equilibrium.

\[
\varepsilon(t) = A \cdot t^n
\]  

(4.1)

After performing several quantitative 1-D simulations, a 2-D isothermal simulation for the alloy with manganese content equal to 9.5 wt.% was carried out. The numerical domain for this simulation corresponds to a square with side equal to 650 μm. The alloy data and the numerical parameters are also shown in Table 2. For this simulation, similarly to the case of 1-D simulations, the interfacial tension of δ-γ interface was assumed to be equal to the interfacial tensions of the δ-L and γ-L interfaces.

Table 2 shows the parameters used in the simulations under directional solidification conditions for the Fe–Mn system. Different simulations were performed with different values of δ-γ interfacial tension in the range presented in this table in order to check: (1) how the δ-γ interfacial tension affects the γ-phase thickness during the steady-state growth on δ-phase (during the peritectic reaction) in the simulation; and, (2) how the simulation results can be compared with the analytical theory presented briefly in Section 3. Thus, the γ-phase thicknesses were measured during the steady-state growth on the δ-phase at a distance of 3.1 μm from the triple-point position. The position of the measurements was defined arbitrarily but considering the interferences of measurements excessively close to the triple-point or extremely far way of this point (the influence of the peritectic transformation – the growth of γ-phase into the liquid and δ-phase). In addition to that, the liquid concentration next to the γ-L interface was determined in the simulations and these determined values were assumed suitable for being utilized as \( x^\gamma_L \) in the analytical model. The other composition terms of the analytical model were determined in accordance with the phase diagram data considering \( x^\delta/L \). Another assumption is that the speed of the γ-phase growth is equal to the pulling speed of the unidirectional solidification on the steady-state. Thus, the analytical values and the simulation results were obtained for directional solidification with thermal gradient equal to 100 K/cm and pulling speed equal to 5.0 and 10.0 μm/s. The numerical domain for this investigation was set equal to 60 μm × 32 μm.

Finally, by utilizing the 2-D approach for directional solidification, simulations of the Fe–C peritectic alloy were performed for different cooling rates obtained by varying the thermal gradient and pulling speed. These simulations were carried out to investigate the amount of the remaining δ-phase at the end of the solidification. Based on it, the simulations had been conducted with the growth of γ-phase on δ-phase until the steady-state being reached and, after that, the complete solidification of the numerical domain has taken place. At the end of the simulations, the amount of each solid phase was determined and the volume fraction of the remaining δ-phase was defined.

In both investigated systems under directional solidification conditions, the shift-back technique of the numerical domain was utilized for all simulations in order to guarantee the occurrence of the steady-state growth of the γ-phase on the δ-phase before obtaining the numerical measurements. This procedure eliminates the interference of the initial transient period on the numerical results.

5. Results and discussion

5.1. Isothermal simulations for Fe–Mn alloys

The first presented results are the evolution of the phases for a hypoperitectic alloy with a manganese content equal to 9.5 wt.% (Fig. 3) and for a hyperperitectic alloy containing 11.0 wt.% of manganese (Fig. 4). In these figures, the total amount of solid phase is represented by small squares and these values were calculated by summing up the δ-phase and the γ-phase percentages. The liquid phase was omitted since it may be determined from the total amount of solid phase.
The percentage of phases in thermodynamic equilibrium at the peritectic temperature, after the phase transformation, is represented by the dashed-lines. The dotted-line of Fig. 4 means the percentage of phases in thermodynamic equilibrium considering the imposed undercooling. This later point can be clarified by utilizing the sketch of Fig. 2. These lines were included in the figures to identify the tendency of the simulated results to follow the thermodynamic equilibrium determined here by the phase diagram data.

The results of Figs. 3 and 4 indicate that the $\gamma$-phase fractions in the beginning of the simulations were equal almost to zero, since this period means the nucleation stage of the new phase. Additionally, with the time evolution, there is simultaneously an increase of the $\gamma$-phase percentage and of the total amount of solid phase, whereas there is a decrease of the $\delta$-phase fraction. It indicates that the $\gamma$-phase is growing into the liquid and into the solid phase simultaneously, exactly as expected for a cooperative peritectic phase transformation [32].

Another observed fact in the results of Figs. 3 and 4 is that the shapes of the curves of phase percentages are asymptotics. It means that, in the beginning of the phase transformation, the growth rate of the $\gamma$-phase is potentially higher than the growth rate in the intermediate or in the final stages of the phase transformation. These asymptotic shapes are commonly observed in phase transformations controlled by diffusion and can be correlated here by the transference of solute from the liquid to the $\delta$-phase through the $\gamma$-phase region. The later point characterizes in the simultaneous movement of the $\delta$-$\gamma$ interface into the $\delta$-phase and of the $\gamma$-L interface into the liquid. The asymptotic behavior of curves observed in the results of Figs. 3 and 4 reinforces the consistency of the numerical model in describing quantitatively the peritectic phase transformation close to the thermodynamic equilibrium for this investigated system. In addition to that, it is important to point out that the peritectic phase transformation under isothermal conditions is strongly influenced and controlled by the solid diffusion inside the $\gamma$-phase. Further discussed details can be found in Ref. [20].

It is also possible to notice in Figs. 3 and 4 that the fraction of phases in the simulations tend to the thermodynamic equilibrium defined by the phase diagram. Nevertheless, the complete thermodynamic equilibrium was not reached for the case of the hypoperitectic alloy (Fig. 3), even though a long simulation time has been utilized. For this simulation, the percentages of $\delta$-phase and $\gamma$-phase at the end of the solidification were equal to 51.5% and 48.5%, respectively. These phase percentages are close to the equilibrium defined by the lever rule at peritectic temperature in the phase diagram (50% for each phase), but they are not equal. This small deviation of the thermodynamic equilibrium can be explained by the kinetic effects, since the peritectic transformation is strongly controlled by the solid diffusion inside the $\gamma$-phase. In the previous work of the authors [20], it was shown that there is a concentration gradient inside the $\gamma$-phase which clarifies the influence of the phase transformation kinetics.

A deviation from the thermodynamic equilibrium was not observed for the case of the hypoperitectic alloy (depicted in Fig. 4). The thermodynamic equilibrium was completely reached for this simulation, as one can observe by the coincidences in the percentages of the $\gamma$-phase, the total amount of solid phase and the thermodynamic equilibrium considering the imposed undercooling. This fact together with the discussed points of the previous paragraphs indicates that the numerical model responds appropriately for simulating the peritectic phase transformation.

In order to define further quantitative results since the isothermal simulations were conducted close to the peritectic temperature (1 K of undercooling), several simulations with concentrations in the range of the peritectic plateau, including the peritectic concentration (10.1 wt.% of Mn), were performed and based on the numerical results, the parameters $A$ and $n$ of...
Eq. (4.1) were determined. The results for the equation parameters versus the chemical composition are depicted in Fig. 5 for the case of the γ-phase thickness expressed in μm and the time in minutes.

One notices by the results of Fig. 5 that, in general, the mathematical parameters of Eq. (4.1) do not vary significantly with the chemical composition from 9.2 to 11.0 wt.% of Mn. The values of A for these chemical compositions are between 2.7 and 4.1 and the values of n between 0.35 and 0.42. The values for both mathematical parameters are in the range observed in experimental works for other metallic alloys [30]. St. John and Hogan [29] have assumed in their investigations that the values of n between 0.35 and 0.57 are acceptable for the proposed analytical model defined by the Eq. (4.1). For the case of the simulation with chemical composition equal to 11.8 wt.% of Mn, a high value of A is observed and a reduced value for n is also noticed. Nevertheless, according to the Wagner [31], these deviations can be explained by the non-perfect homogenization of the liquid and/or of the peritectic phase. This later fact may also be used to explain why n of Eq. (4.1) deviates from 0.5 (a parabolic law).

Fig. 6 shows the results of a 2-D isothermal simulation of a hypoperitectic alloy with manganese content equal to 9.5 wt.%. The δ-phase is represented by the dark gray, the liquid by the light gray and the γ-phase by the back color. Small nuclei of γ-phase were positioned randomly in different regions of the δ-liquid interface in the beginning of the peritectic numerical simulation (Fig. 6a). The initial nuclei have grown around the δ-phase firstly, characterizing the peritectic reaction, and after that into the liquid and into the δ-phase simultaneously, characterizing the peritectic transformation. This second stage is clearly shown in the results of Fig. 6b–d.

The solid percentage presented in Fig. 6d is equal to 99.6% with 65.6% of the δ-phase and 34.1% of the γ-phase and, 50% of each phase would be expected according to the lever rule at the peritectic temperature. This deviation can be justified by the kinetic effects similar of those points already discussed for the 1-D case. Additionally, this complete solidified structure can be considered in a non-equilibrium state, which is commonly found in continuous cooling processes (e.g. continuous casting) with a remaining amount of δ-phase at the end of the solidification. Finally, another observed fact is that the branched structures (similar to the secondary dendrite arms in one-phase solidification) between the δ-phase and the γ-phase tend to get rough with the progress of the peritectic reaction. This fact can be confirmed by comparing Fig. 6b–d.

5.2. Directional solidification for the peritectic alloy in the Fe–Mn system

In this part of the present investigation, the comparison of the γ-phase thicknesses during the peritectic reaction is presented for the case of values measured directly in the numerical domain and for the cases of values estimated by the analytical model of the section 3. The selected alloy was a Fe–Mn alloy with chemical composition equal to the peritectic concentration (10.1 wt.% of manganese) and Fig. 7 shows a numerical result at an intermediate stage of γ-phase growth on δ-phase. This numerical result was for a simulation with the δ-γ interfacial tension of 0.59 J/m². The result of this figure displays clearly the occurrence of the peritectic reaction and, at the same time, shows the position of the γ-phase thickness measurements in the numerical simulations (see sketch of Fig. 1 to identify ε, the γ-phase thickness).

For this investigation, two different pulling speeds were utilized, 5.0 and 10.0 μm/s. The results of the γ-phase thicknesses for simulations and for the estimations through the analytical model are presented in Fig. 8. Based on the results of this figure, the simulations with FFM and the estimated results utilizing the analytical model are comparable for both utilized pulling speeds, even though small differences can be observed. The differences between the simulation results and the analytical estimations have the same magnitude of those observed in the experimental works [21].

Another point observed in the results of Fig. 8 is that the theoretical values of γ-phase thickness estimated by the analytical model for different values of the δ–γ
interfacial tension are almost constant for the case of pulling speed equal to 10.0 μm/s. The same observation cannot be directly identified for the case of pulling speed equal to 5.0 μm/s. The analytical values for this later pulling speed have a small increase with the rise of δ–γ interfacial tensions, whereas the simulated values have the same qualitative behavior, even though with a more pronounced increase.

5.3. The estimated remaining δ-phase in peritectic phase transformation of the Fe–C system

After noticing the occurrence of a metastable thermodynamic equilibrium for the isothermal simulations in the Fe–Mn system with the presence of an amount of remaining δ-phase at the end of the solidification (see Section 5.1), this point motivates the development of an investigation in the Fe–C system with peritectic phase concentration (0.172 wt.% of carbon) and under different cooling rate conditions. This metastable state may be observed in the continuous cooling processes and this Fe–C system is a basic system for a large amount of steel products. Therefore, simulations utilizing the unidirectional solidification set-up, similar of that presented in Section 5.2,
were performed and the amount of the remaining δ-phase at the end of the solidification was determined. The results of the remaining δ-phase volume fraction versus the cooling rate are presented in Fig. 9. There are also in the figure a suggested function obtained by a regression of the numerical data and the coefficient of determination, $R^2$.

The presence of the remaining δ-phase can be noticed for the whole range of the explored cooling rates, according to the results of Fig. 9. For low cooling rates, the amount of the remaining δ-phase is reduced and, for more intensive cooling rates, the percentage of the remaining δ-phase is higher. According to the investigated range of cooling rates, the remaining δ-phase has varied from 6.4% for cooling rate equal to 0.1 K/s to 11.1% for 2.4 K/s. The increase of the remaining δ-phase with the rise of cooling rate is not linear and the suggested function here for this phenomenon is a power function. A suggested function for estimating the volume fraction of remaining δ-phase as investigated here has not yet been extensively explored utilizing a similar approach to the knowledge of the present authors.

Another point that can be mentioned is that the range of explored cooling rate, from 0.1 to 2.4 K/s, is similar of those observed in the ingot casting area and in the intermediate to final stages of solidification in continuous casting processes. Therefore, the suggested equation to estimate the remaining δ-phase can also be utilized in experimental fields or technical approaches. The remaining δ-phase may transform into the γ-phase in the absence of a liquid phase, and this aspect is of considerable technological relevance, since a volume contraction of about 0.5% is observed in steels during the phase transformation from δ-phase to γ-phase. This volume reduction yields to strains and stresses in the material at a low ductility temperature range [33].

6. Conclusions

The present approach is consistent with the laws of thermodynamic equilibrium and kinetics, since the numerical simulations, in both aspects, have responded in a proper way when compared to the basic theory of the peritectic phase transformation. This fact was observed in the results of all simulations and the points which can be highlighted for supporting this argumentation are: (1) the asymptotic shape of the phase fraction curves with time evolution for the isothermal solidifications close to the peritectic temperature; (2) the mathematical coefficient $A$ and the exponent $n$ of Eq. (4.1) obtained based on the simulation results being in the same range of those observed in experimental works; (3) the γ-phase thickness measured during the steady-state growth of γ-phase on the δ-phase being completely comparable with an analytical model present in the literature; and, (4) the occurrence of a metastable state at the end of the solidification with the presence of an amount of remaining δ-phase during continuous cooling processes.

The comparison between the analytical theory and the simulation results (in the Fe–Mn system) for the γ-phase thickness during the peritectic reaction indicates that the analytical theory found in the literature provides a fair approximation to describe the present phenomenon. The phase-field approach, by definition, is able to solve in a proper way the Stefan’s problem and, thus, it would be expected to yield results close to the reality than the analytical theory which does not contemplate precisely this point in its formulation. Therefore, in spite of the fair agreement between the two approaches, the
phase-field approach should be preferred for a precise estimation of the residual amount of δ-phase.

A mathematical relation between the cooling rate and the remaining δ-phase amount at the end of the solidification in an alloy with peritectic concentration in the Fe–C system was determined based on the simulation results and this relation supplied a reasonable estimate for the present purpose. This mathematical relation may be validated in the future utilizing experimental works and/or being utilized directly in experimental fields or technical processes of steel solidification, since the metastable δ-phase at the end of solidification for these peritectic steels is undesired due to the increases of the strain and stress levels in the material at a low ductility temperature range.

Finally, based on the fact that the quantitative results of this investigation were reliable, the present approach may be utilized for other investigations of the microstructure evolution in peritectic binary alloys under isothermal or under directional solidification conditions, since some aspects of the microstructure evolution during the peritectic phase transformation are technically difficult and even costly intensive to investigate in experimental works.

Conflicts of interest

The authors declare no conflicts of interest.

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