

**NUMERICAL SIMULATION OF NON ISOTHERMAL DENDRITIC GROWTH AND
MICROSEGREGATION DURING THE SOLIDIFICATION PROCESS FOR QUATERNARY ALLOYS
(Fe-C-Mn-P)**

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***Resumo:** Solidification is the main phenomenon taking place during casting. For this reason, solidification studies are not just mandatory; they truly are a powerful industrial tool. For conventional technologies, thorough understanding and control of the solidification process opens wide perspectives in terms of its economic potential, since it provides the shortest distance from metal input to final product. Events like nucleation and growth of dendritic structures — which, in the absence of a tight control, may compromise the final output or even halt the manufacturing process altogether. Therefore, solidification and the main structures arising from it — the dendrites — are extremely important from a practical standpoint, in that they exert a strong influence on the properties of the products. Even more detailed numerical models using classical equations can hardly resolve complicated two- and three-dimensional dendrite structures. Also, methods based on classical transport equations are found to be limited when dealing with meta-stable states. Pure substances provide one such example, when the solidification front advances through a super-cooled liquid phase. Another case is that of alloy solidification, for instabilities of the advancing front can occur owing to constitutional super-cooling. In these instances, the solid-liquid interface may develop a complex geometry, locally dependent on curvature, solidification speed, and possibly anisotropy. In particular, the Phase-Field Method has garnered wide acceptance, given its ability to simulate the solidification process in the presence of a complicated solid-liquid interface. Usually, in phase-field works, solutions to the equations are obtained by divided differences. For alloys, dendrite growth is considered at constant temperature or constant cooling rate. In our work, all equations were solved numerically with recourse to the Finite-Volume Method. The reason for such a choice lies in that this is a conservative method. For the transient term in the energy conservation equation, an implicit scheme is used, owing to its unconditional numerical stability regardless of the size of the time step used. In all of our simulations, a single, stable, solid nucleus is considered to have been previously added to the liquid domain. Moreover, for applying the Phase-Field Method to the solidification of Fe-C-P-Mn quaternary alloys, we prescribe as initial conditions the temperature and solute concentration, taking into account surface tension and crystal anisotropy effects. The study of the effect of phosphorus on steel was selected because even in small quantities it influences steel quality greatly. Phosphorus is generally regarded as a harmful component, given that it tends to render steels fragile, especially high-carbon steels or when its content goes beyond certain acceptable limits. For this reason, the maximum admissible phosphorus content is specified. While manganese eliminates the impurities from steel and change its mechanical properties, conferring malleableness to final product. This study aims to solve numerically the equations of the Phase-Field, energy and concentration of solute in a two-dimensional system focusing the determination of the morphology of dendrites generated in the solidification process of multicomponent alloys (Fe-C-P-Mn), for different cooling conditions and concentrations.*

***Palavras-chave:** solidification, simulation, dendrite*

1. INTRODUCTION

The phase-field model is known to be a powerful tool for describing the complex pattern evolution of the interface between mother and new phases in nonequilibrium state because all the governing equations are written in unified manner in the whole space of system. The phase-field variable, ϕ ; changes steeply and smoothly at the solid-liquid interface region, which avoids direct tracking of the interface position. Therefore, the model can be regarded as a type of a diffuse interface model, which assumes that the interface has a finite thickness and that the physical properties of the system vary smoothly through the interface. It is efficient, especially in numerical treatment, because all the governing equations are written in a unified form without distinguishing the interface from the solid or from the liquid phase. In the model, the phase-field, $\phi(x,y,t)$; characterizes the physical state of the system at each position and time: $\phi = +1$ for the solid, $\phi = 0$ for the liquid, and $0 < \phi < +1$ at the interface. The phase-field model has attracted many scientists due to its ability in describing the complex pattern formations in phase transitions such as dendrites. It is a useful method for realistically simulating microstructural evolution involving diffusion, coarsening of dendrites and the curvature and kinetic effects on the moving solid-liquid interface.

The model was originally proposed for simulating dendrite growth in undercooled pure melts (Kobayashi, 1993; Kim et al., 1999; Furtado et al., 2006), and has been extended to solidification of alloys (Lee and Suzuki, 1999; Ode and Suzuki, 2002).

A phase-field model is proposed for simulation of microstructure and solute concentration during the solidification process of Fe-C-P-Mn quaternary alloys.

In present paper, we study both the effects of partition coefficient and diffusivity of solute on the microstructural evolution during the simulation of solidification process. The partition coefficient and diffusivity are extremely important from a practical standpoint, because exert a strong influence on the morphology dendrite.

Additionally, we apply the model for quaternary alloys to: a) analysis of the solidified fraction with time during the solidification process; b) estimate of solute (carbon, phosphorus and manganese) in the solid and; c) influence of solute concentration on the dendrite morphology.

2. Phase-field model for Multicomponent Alloy

In the phase-field model, the state of the entire microstructure is represented continuously by a single variable known as the order parameter ϕ . For example, $\phi = 1$, $\phi = 0$ and $0 < \phi < 1$ represent the solid, liquid and interface respectively. The latter is therefore located by the region over which ϕ changes from its liquid-value to its solid-value. The range over which it changes is the width of the interface. The set of values of the order parameter over the whole microstructure is the phase field. For simulation of microsegregation in quaternary alloys during solidification process, we used five equations: one for energy, one for phase-field and three equations for solute concentrations (carbon, phosphorus and manganese). The energy equation to be integrated is (Furtado et al., 2006)

$$\frac{\partial T}{\partial t} = D\nabla^2 T + \frac{\Delta H}{c_p} h'(\phi) \frac{\partial \phi}{\partial t} \quad (1)$$

The term on the left-hand side represents the time variation of the specific thermal energy divided by the constant pressure specific heat. The first term on the right-hand side is the divergence of the heat transfer by heat diffusion (conduction) divided by the product of specific mass and constant pressure heat capacity, where D is the thermal diffusivity and T representing the temperature. The second term on this side is a source, where C_p is the specific heat at constant pressure, ΔH measures the latent-heat variation around the interface and $h'(\phi)$ is the derivative of the so-called "smoothing" function, to be defined later. The derivative $\partial \phi / \partial t$ is the time-and-space rate of variation of the phase-field variable, ϕ .

Ode et al. (2000) proposed a solute transport and phase equation for modeling and simulation of solidification process in ternary alloys, in present paper; we extended these equations for solidification with multicomponent alloys (Fe-C-P-Mn). The time evolution equation of the phase-field ϕ is described by:

$$\begin{aligned} (1/M)(\partial \phi / \partial t) = & \varepsilon^2 \nabla^2 \phi - w g'(\phi) \\ & + h'(\phi) \frac{RT}{V_m} \text{Ln} \left\{ \frac{\left[1 - (c_{CS}^e + c_{PS}^e + c_{MnS}^e) \right] \left[1 - (c_{CL} + c_{PL} + c_{MnL}) \right]}{\left[1 - (c_{CL}^e + c_{PL}^e + c_{MnL}^e) \right] \left[1 - (c_{CS} + c_{PS} + c_{MnS}) \right]} \right\} + noise \end{aligned} \quad (2)$$

The evolution of the solid nucleus with time ($\partial \phi / \partial t$) is assumed to be proportional to the variation of the free-energy functional with respect to the order parameter, ϕ . The terms of the phase equation are derived from this free-energy functional, which must decrease during any solidification process, as indicated in the article by Furtado et al. (2006). In Eq. (2), M quantifies the phase-field mobility. The product $\varepsilon^2 \nabla^2 \phi$ is a diffusivity term. The next component of the equation, $w g'(\phi)$, factors in the excess free energy arising from surface tension around the interface. The last product on the right-hand side translates the driving force behind the solidification process. Here, R is the gas constant and V_m , the molar volume. The arguments to the natural logarithms, c_{CS}^e , c_{PS}^e and c_{MnS}^e are, respectively, the equilibrium concentrations of carbon, phosphorus and manganese in the solid region. Likewise, c_{CL}^e , c_{PL}^e and c_{MnL}^e

represent their corresponding equilibrium concentrations in the liquid phase. Their respective ordinary concentrations in the liquid and solid regions are denoted, by the trios, c_{CL} , c_{PL} and c_{MnL} , and c_{CS} , c_{PS} and c_{MnS} . The noise term in the right-hand side of the phase-field equation will be explained later.

The solute concentrations in both solid and liquid regions are calculated, as following:

$$\frac{\partial c_C}{\partial t} = \nabla \left\{ D_C(\phi) \left\{ [1-h(\phi)] \frac{c_{CL} [1-(c_{CL} + c_{PL} + c_{MnL})]}{1-(c_{PL} + c_{MnL})} + h(\phi) \frac{c_{CS} [1-(c_{CS} + c_{PS} + c_{MnS})]}{1-(c_{PS} + c_{MnL})} \right\} \cdot \nabla \text{Ln} \left[\frac{c_{CL}}{1-(c_{CL} + c_{PL} + c_{MnL})} \right] \right\} \quad (3)$$

$$\frac{\partial c_P}{\partial t} = \nabla \left\{ D_P(\phi) \left\{ [1-h(\phi)] \frac{c_{PL} [1-(c_{CL} + c_{PL} + c_{MnL})]}{1-(c_{CL} + c_{MnL})} + h(\phi) \frac{c_{PS} [1-(c_{CS} + c_{PS} + c_{MnS})]}{1-(c_{CS} + c_{MnS})} \right\} \cdot \nabla \text{Ln} \left[\frac{c_{PL}}{1-(c_{CL} + c_{PL} + c_{MnL})} \right] \right\} \quad (4)$$

$$\frac{\partial c_{Mn}}{\partial t} = \nabla \left\{ D_{Mn}(\phi) \left\{ [1-h(\phi)] \frac{c_{MnL} [1-(c_{MnL} + c_{PL} + c_{CL})]}{1-(c_{CL} + c_{PL})} + h(\phi) \frac{c_{MnS} [1-(c_{MnS} + c_{PS} + c_{CS})]}{1-(c_{CS} + c_{PS})} \right\} \cdot \nabla \text{Ln} \left[\frac{c_{MnL}}{1-(c_{MnL} + c_{PL} + c_{CL})} \right] \right\} \quad (5)$$

In these equations D_C , D_P and D_{Mn} are the carbon, phosphorus and manganese diffusivities in the solid and liquid regions. The model used here takes into account solute diffusivity in the liquid and interface regions.

The system we focus on is the solid nucleus plus the liquid around it, plus the interface. For the phase-field model, this system is continuously represented by the single phase-field variable, ϕ . A value $\phi = +1$ is associated with a solid nucleus. On the other hand, $\phi = 0$ corresponds to the liquid medium. Finally, a value between 0 and +1 indicates the interface. The smoothing function $h(\phi)$ and the function $g(\phi)$, which models the surface tension effect around the interface, are defined, respectively, by (Furtado et al., 2006)

$$h(\phi) = \phi^3 (10 - 15\phi + 6\phi^2) \quad (6)$$

$$g(\phi) = \phi^2 (1 - \phi)^2 \quad (7)$$

Equations (6) and (7) are widely employed in phase-field works. Notice $h'(\phi)$ and $g'(\phi)$ are zero for both $\phi = 0$ (liquid region) and $\phi = +1$ (solid region). This ensures that only at the interface will the second and third terms in Eq. (2) be nonzero. Moreover, a commonly resorted way of including anisotropy in the model is to regard ε in Eq. (2) as dependent on a so-called "growth angle," θ . The growth angle reflects the orientation of the normal to the interface with respect to the x axis, i.e., the longitudinal interface advance direction (Furtado, 2006):

$$\varepsilon(\theta) = \varepsilon_0 \{1 + \delta_\varepsilon \cos [j(\theta - \theta_0)]\} \quad (8)$$

where δ_ε gauges the anisotropy. The value j controls the number of preferential growth directions. For example, with $j = 0$ we shall be looking at a perfectly isotropic case, while $j = 4$ is indicative of a dendrite with four preferential growth directions. Orientation of the maximum-anisotropy interface is identified by the θ_0 constant of Eq. (7). Furthermore, ε_0 , in that equation, and w , in Eq. (2), are model parameters associated with interface energy (σ) and thickness (λ), respectively, according to the following expressions (Furtado, 2006):

$$2\lambda = \int_{0,1}^{0,9} \frac{dx}{d\phi_0} d\phi_0 = 2.2\sqrt{2} \frac{\varepsilon_0}{\sqrt{w}} \quad (9)$$

$$\sigma = \varepsilon_0^2 \int_{-\lambda}^{+\lambda} \left(\frac{\partial \phi_0}{\partial x} \right)^2 dx = \frac{\varepsilon_0 \sqrt{w}}{3\sqrt{2}} \quad (10)$$

Also from Furtado (2006), the phase-equation mobility, M , is computed as

$$\frac{1}{M} = \frac{\varepsilon_0^3}{\sigma\sqrt{2}w} \left[\frac{1}{D_{1i}} \xi_1(c_{1L}^e, c_{1S}^e) + \frac{1}{D_{2i}} \xi_2(c_{2L}^e, c_{2S}^e) + \frac{1}{D_{3i}} \xi_3(c_{3L}^e, c_{3S}^e) \right] \quad (11)$$

where each of the ξ_j is obtained from

$$\xi_j = \frac{RT}{V_m} (c_{jL}^e - c_{jS}^e)^2 \times \int_0^1 \left\{ \frac{h(\phi_0) [1 - h(\phi_0)]}{[1 - h(\phi_0)] c_{jL}^e (1 - c_{jL}^e) + h(\phi_0) c_{jS}^e (1 - c_{jS}^e)} \times \frac{d\phi_0}{\phi_0 (1 - \phi_0)} \right\} \quad (12)$$

In Eqs. (11) and (12), L and S stand for liquid and solid, respectively.

To simulate growth of an asymmetrical dendrite, it is necessary to introduce a noise term in the right-hand side of the phase-field equation. A usual expression for this noise, as indicated by Furtado (2006), is

$$noise = 16ar\phi^2(1 - \phi)^2 \quad (13)$$

with r a random number between -1 and $+1$. The a parameter is the noise amplitude. Maximum noise corresponds to $\phi = 0.5$, at the center of the interface, whereas at $\phi = 0$ (liquid region) and $\phi = +1$ (solid region) there occurs no noise. That is to say, noise is generated at the interface.

3. RESULTS AND DISCUSSIONS

We introduce phase-field results for the carbon, phosphorus and manganese concentrations in the solid region. These estimates shall later be compared with Scheil equation and Clyne-Kurz equation. Table 1 presents the physical properties of the alloy used in the computations that follow.

Table 1. Physical properties of alloy (Ode et al., 2000).

Property	C	P	Mn	Fe
Partition coefficient	0.17171	0.28958	0.7213	-----
Slope of liquidus line, m_e (K/mol)	1772.77	2059.54	495.32	-----
Diffusivity of solute in the liquid, D_L (m ² /s)	2.0×10^{-8}	1.7×10^{-9}	1.0×10^{-9}	-----
Diffusivity of solute in the solid, D_S (m ² /s)	6.0×10^{-9}	5.5×10^{-11}	3.0×10^{-13}	-----
Interface energy, σ (J/m ²)	-----	-----	-----	0.204
Melting temperature, T_m (K)	-----	-----	-----	1810
Molar volume, V_m (m ³ /mol)	-----	-----	-----	7.7×10^{-6}

Table 2 presents the parameters used in the phase-field method.

Table 2. Computational parameters.

Anisotropy, δ_ϵ	0.05
Interface thickness, ϵ_0 (J/m) ^{1/2}	1.05×10^{-4}
Surface tension, w (J/m ³)	6.73×10^7
Interface mobility, M (m ³ /sJ)	0.166
Grid spacing, $\Delta x = \Delta y$ (m)	3.0×10^{-8}
Time-step length, Δt (s)	1×10^{-8}
Noise amplitude, a	0.025

The boundary condition adopted for the phase-field method (ϕ) in this work is a zero-flux condition. Adiabatic boundary conditions were used for integrating the energy equation. In preparing this article, the authors placed appreciable attention on the choice of a suitable computational grid. Even not too Sharp an interface may still be fine enough to capture correctly the phenomena that occur there. Thus, a square mesh (dimensions: $\Delta x = \Delta y = 3 \times 10^{-8}$ m) has been used. Figure 1 shows the evolution of the solid fraction (F_S) with time for an initial temperature of 1780 K. This solid fraction is given by the ration of the solid control volume to the total control volume of the domain, as shown in the following expression:

$$F_s = 100(V_s/V_l)$$

(14)

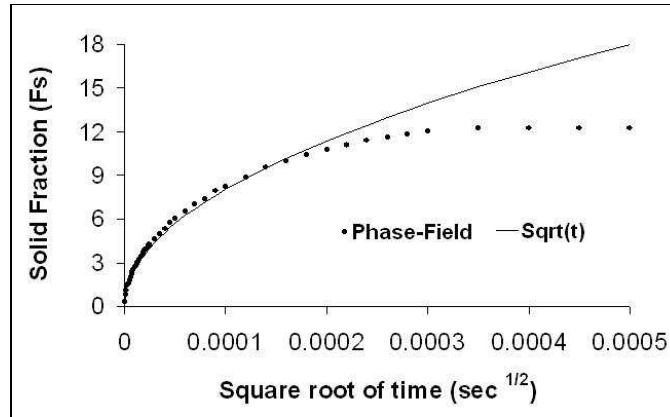


Figure 1. Solid fraction (FS) versus time.

A thin solid layer was added at the left boundary of the rectangular domain. In the next figure, the solid line represents fit, which is dependent upon a function of the square root of the time, whereas the points represent the values computed with the phase-field model. In Fig. 1, the solid fraction (F_s) is seen to increase faster at the onset of solidification. This rate then gradually diminishes towards completion of the solidification process. This slowing down is due to a reduction of interface mobility as the temperature increases. Given that we are considering adiabatic boundary conditions, owing to liberation of latent heat during the change of phase, an increase of the temperature occurs as a consequence of the reduction of the interface mobility. Traditionally, one assumes that the solid fraction (F_s) is proportional to the square root of time, as any diffusion controlled growth process (Chalmers, 1964).

Figure 2 exhibit the results of the carbon concentrations. We compare the results of phase-field calculation in 1-D with the predictions by Scheil's equation and by Clyne-Kurz's equation. The initial temperature of computational domain is equal 1780K. For the calculations of the solute concentrations we assumed isothermal solidification process. We added a thin solid layer of concentration C_0 at the left boundary of the computation domain. The calculated profile for carbon agree better with the Clyne-Kurz's equation than Scheil's equation when the solid fraction is above 0.5, as shown in figure 2, this is because Clyne-Kurz model assumed the back-diffusion. Analytical model of Scheil admitted that diffusion in the solid phase is completely neglected and complete mixing of the solute in liquid phase is assumed. C_S is the concentration in the solid at the solid/liquid interface and C_0 is the initial concentration of solute. We can see that phase-field-based results lie above those obtained with Scheil's equation; the little difference in early stage of solidification would be the effect of the initial transient because of small diffusivity in the solid. These results show that the phase-field model calculate the same solid concentration in the solid/liquid interface for carbon as that Clyne-Kurz's equation can estimate. Both models Scheil and Clyne-Kurz, however, cannot predict the composition profile in solid. The phase-field model can simulate not only concentration in solid but also a concentration profile in liquid during the solidification process.

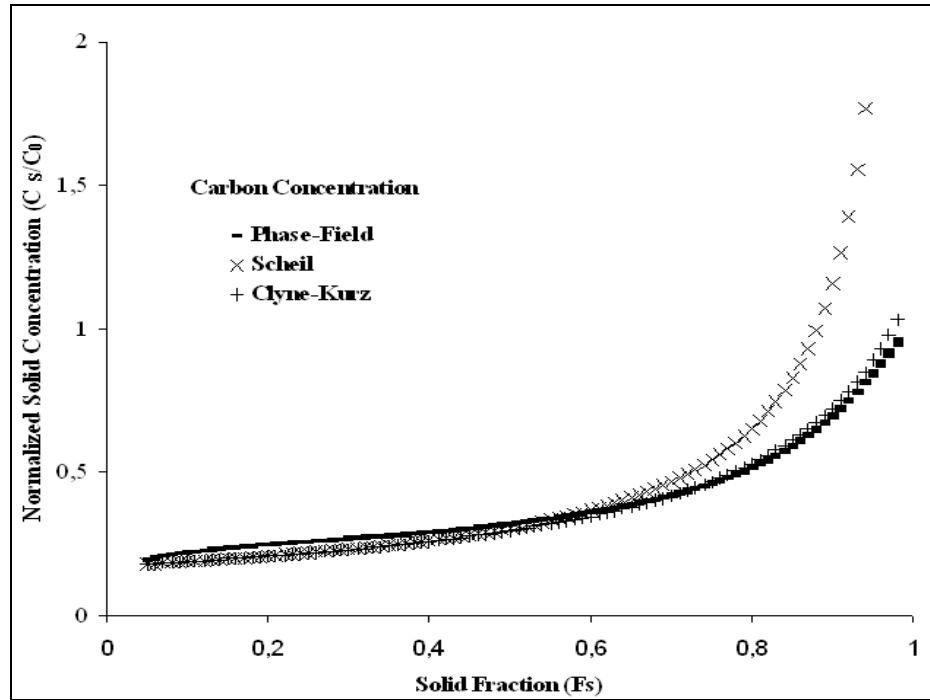


Figure 2. Comparison of solutes concentration, as evaluated via the phase-field model, with Scheil's equation and Clyne-Kurz's equation.

We analyze non isothermal dendrite growth in two-dimensional system. The dendrite shapes of Fe- 3.93×10^{-3} mol% C- 4.65×10^{-5} mol% P- 7.58×10^{-3} mol% Mn and Fe- 8.93×10^{-3} mol% C- 4.65×10^{-5} mol% P- 7.58×10^{-3} mol% Mn in quaternary alloys at 1780 K are shown in Fig. 3. The secondary arms develop well and the arm spacing becomes narrow with an additional carbon, Figures 3(a) and 3(b), because the carbons is likely to enriched at the interface and reduce the interface stability.

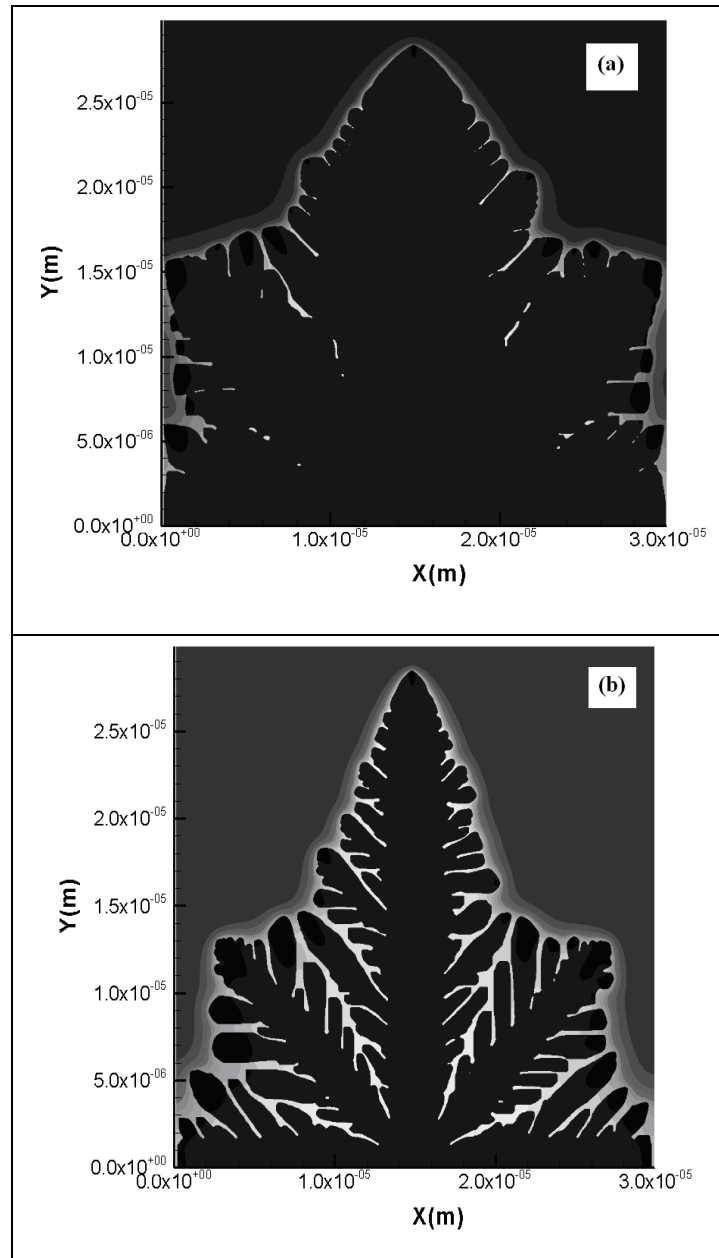


Figure 3. Carbon and phosphorus solute concentration fields.

We analyze non isothermal dendrite growth in two-dimensional system. The shapes of Fe-3.93x10⁻³mol%C-4.65x10⁻⁵mol%P-7.58x10⁻³mol%Mn quaternary alloy at 1775 and 1785 K are shown in Fig. 4. The secondary arms develop well and the arm spacing becomes increase with the decrease of super cooling ($\Delta T = T_{melting} - T_0$), from 36 K to 26 K. It occurs because decrease of super cooling reduces the mobility of solid/liquid interface. The change in the super cooling is proportional to the phase-field mobility. The morphology dendrite depending on the super cooling.

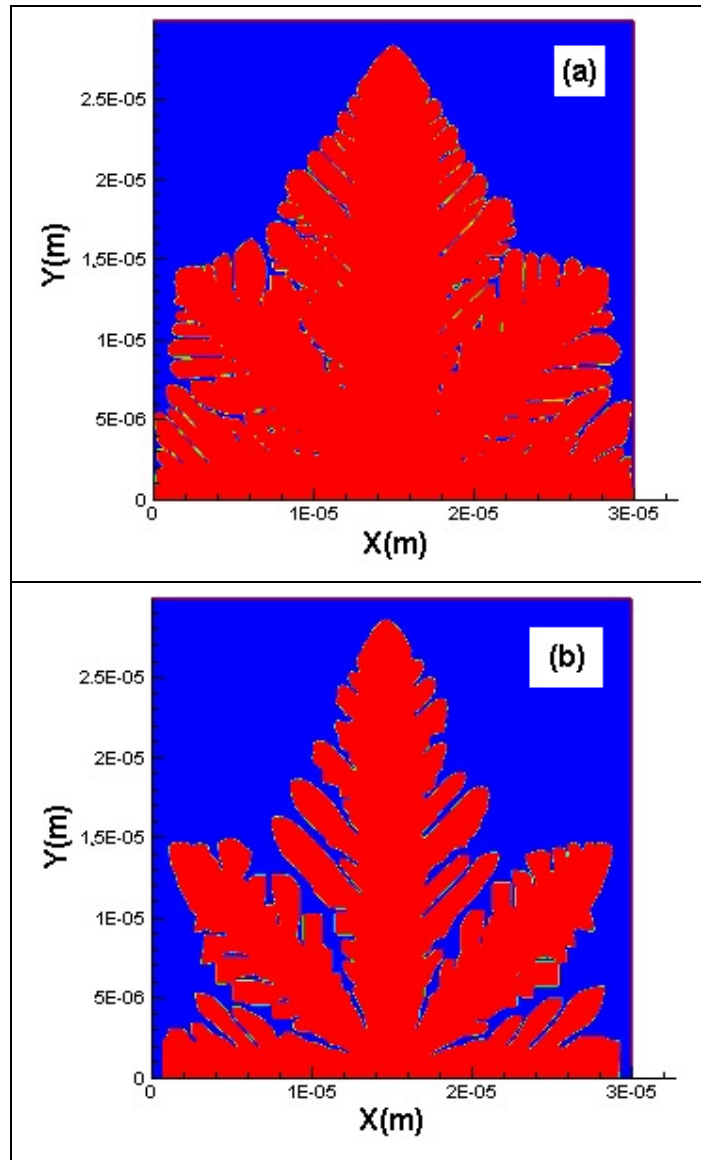


Figure 4. Shape of non isothermal dendrite.

4. Conclusions

Results for solid fraction (F_s) against time at solidification onset are in agreement with kinetic theory of solidification process. That is, the solid fraction is roughly proportional to the square root of time. The slowing down of solidification rate is due to a reduction of interface mobility as the temperature increases. Given that was considered adiabatic boundary conditions in present calculations.

Using the phase field model, the solutes concentrations was calculated for quaternary alloys and compared with the analytical models. The concentration profiles show good agreement with those of Clyne-Kurz equation. Solute concentrations as calculated by phase field model differ from values obtained with Scheil's equation. This occurs because our model takes into account solute diffusivity in the solid and liquid phases.

For tow-dimensional calculations, non isothermal dendrite growth is simulated for Fe-C-P-Mn alloys, which was reproduced dendrites similar to the ones found in experiments reported in the literature, complete with primary and secondary arms. The change in carbon concentration affects the interface mobility and the dendrite shape. The secondary arm spacing significantly changes with the super cooling.

The results seem to be quite reasonable and show the wide potentiality of phase field model for simulations of solidification process.

5. ACKNOWLEDGEMENTS

The authors wish to thank Universidade Federal Fluminense (UFF) and, in particular, its School of Industrial and Metallurgical Engineering (EEIMVR), for financial support and the necessary infrastructure for developing this research.

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