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Simulation of the Dendritic Growth Velocity for Binary Alloy Al-Cu in the Undercooled System

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ABSTRACT

The phase-field model was applied to simulate the solidification kinetics to undercooled Al-Cu alloy. The relationships between material properties and model parameters are presented. The diffusivity of solute in the solid region and liquid and liquidus temperature are calculated during the simulation of solidification process. As an example, the two-dimensional computations for the dendritic growth in Al-Cu binary alloy have been performed. The dendritic morphology calculated by phase-field model showed features that are commonly found in experiments on the solidification. The concentration profiles of solute calculated in the solid region and liquid are not completely horizontal, showing evidence of microsegregation. The velocity of the dendrite tip and solute concentration at the interface front are calculated. It is found that the tip velocity is greatly concentration dependent around interface. In order to validate the growth kinetics predicted by this model tests have been performed for comparison with Stefanescu's model. The present work based results show good agreement with those obtained by Stefanescu. The dependence of growth velocity on the initial concentration and super-cooling are also demonstrated.

Keywords: Solidification; Undercooling; Kinetics; Phase-field model; Al-Cu.

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1. Introduction

Solidification of undercooled melts has attracted much attention, since it is attractive to study the non-equilibrium dendritic growth phenomena and the formation of resulting structures. It, in turn, is essential for the development of improved methods for quality castings. The solidification of alloys involves heat, fluid flow and the transport of solute, which influence the development of both the macrostructure and the microstructure. The prediction of these structures, 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. As a consequence, solidification is one of the most important specialties in Metallurgy and Materials Science. In-the-mold solidification of a metal, opposite to what might at first be surmised, is not a “passive” process in any way. On the contrary, the metal undergoes a liquid-to-solid transformation of very dynamic nature. In its course, events take place – 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. Such events can originate several types of material heterogeneities, which drastically affect the metallurgical quality of the final product. However, in the many cases, analytical solutions to the equations of motion for the solid–liquid interface, using techniques such as boundary integral methods, Khachaturyan,^[1] cannot be found and recourse must be made to numerical techniques.

One technique which over the last few decades has received the most attention is that of phase-field simulation, in which a nonconserved order parameter (ϕ), which encodes the phase state of the material, is defined over the whole domain as mentioned by Ferreira et al.^[2] The phase-field model has recently emerged as the most powerful computational tool for simulating complicated dendrite growth. Because of its flexibility in treating complex geometries and topological changes, the phase-field model has been used widely in modeling microstructural evolution during various phase transformations, grain growth and, most recently, plastic deformations. In this present paper, a phase-field model is employed to analyze the kinetics of solidification in Al-Cu system. The divided-differences method is used

for solution of the equations, keeping a constant cooling rate during numerical simulation of the solidification. The phase-field model is employed to analyze the kinetics of solidification in Al-Cu system. In contrast to the previous models, this model considers the diffusivity of solute depends on temperature field and the liquidus temperature is calculated by non-uniform concentration distribution. This seemingly minor difference constitutes the main new feature of the present model and it is discussed in more detail in next section. The model enables us to predict the interface velocity quantitatively and to examine the effect of the radius of dendrite tip, concentration and super-cooling on the kinetics of growth dendritic during solidification process.

2. Phase-field Modeling for Al-Cu System

In phase-field models, the state of the domain is customarily represented by a distribution of the single variable known as the “order parameter” or “phase-field variable,” here represented by the Greek letter ϕ . In this study, it is assumed that the solid state corresponds to a value of +1 for the order parameter, while, in the liquid region, ϕ is taken to be 0. The region through which ϕ decreases from +1 to 0 is defined as the solid-liquid interface. For simulation of microstructures in binary alloys during solidification, we used two equations: one for solute concentrations, the other for the phase field itself. Following Ode et al.,^[3] the first equation takes the form

$$\frac{1}{M} \frac{\partial \phi}{\partial t} = \varepsilon^2 \nabla^2 \phi - W g'(\phi) + \frac{K}{V_m} h'(\phi) \ln \left[\frac{(1 - c_S^e)(1 - c_L)}{(1 - c_L^e)(1 - c_S)} \right] \quad (1)$$

where “ \ln ” stands for the principal argument of the natural logarithm of the fraction function within the square brackets. As for the phase-field equation, those authors propose

$$\frac{\partial c}{\partial t} = \nabla \cdot \left\{ D(\phi) [(1 - h(\phi))(1 - c_L)c_L + h(\phi)(1 - c_S)c_S] \nabla \ln \left(\frac{c_L}{1 - c_L} \right) \right\} \quad (2)$$

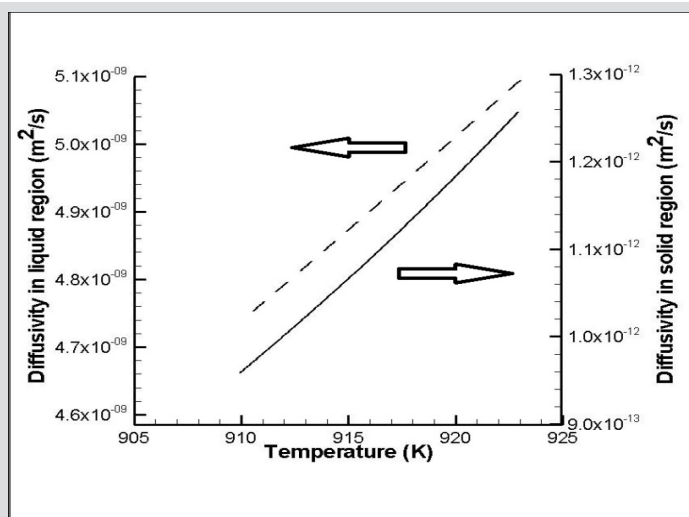
where $h(\phi) = \phi^2(3 - 2\phi)$, $g(\phi) = \phi^2(1 - \phi)^2$, and the subscripts S and L stand for solid and liquid, respectively. M and ε are phase-field parameters; $D(\phi)$ is the solute diffusion coefficient. These phase-field parameters are related to the interface energy, σ_ϕ , whereas the interface width, 2λ , is the distance over which ϕ changes from 0.1 to 0.9. Notice, furthermore, that M is also re-

Table 1. Model parameters (Ferreira et al. [2]).

| | |
|--|---|
| Number of preferential growth directions, j | 4 |
| Height of the double-well potential, W | $2.01 \times 10^{+6} \text{ J m}^{-3}$ |
| Coefficient of phase-field gradient energy term, ε_0 | $5.57 \times 10^{-4} [\text{J m}^{-1}]^{1/2}$ |
| Noise amplitude factor, α | 0.03 |
| Anisotropy constant, δ_ε | 0.03 |
| Grid spacing, Δx | $1.5 \times 10^{-7} \text{ m}$ |
| Grid spacing, Δy | $1.5 \times 10^{-7} \text{ m}$ |
| Time step, Δt | $1.5 \times 10^{-6} \text{ s}$ |

Table 2. Material properties of Al-0.0196%molCu system (Ferreira et al. [2]).

| | |
|---|---|
| Interface energy, σ_0 | 0.093 J m^{-2} |
| Kinetic coefficient at interface, μ_k | $1 \text{ m s}^{-1} \text{ K}^{-1}$ |
| Liquidus temperature, T_L | 923 K |
| Molar volume, V_m | $1.095 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ |
| Partition coefficient, | 0.14 |
| Slope of liquidus line, m_e | 672 K mol^{-1} |
| Diffusivity in solid region, D_s | $3.0 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$ |
| Diffusivity in liquid region, D_L | $3.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ |

**Figure 1.** Variation of diffusion coefficient in liquid (D_L) and solid (D_s) as a function of temperature.

lated to the kinetic coefficient, β , defined to be the inverse of the usual linear kinetic coefficient, μ_k . From Salvino et al.,^[4] these are obtained as

$$\sigma = \frac{\varepsilon_0 \sqrt{W}}{3\sqrt{2}} \quad (3)$$

$$2\lambda = 2.2\sqrt{2} \frac{\varepsilon_0}{\sqrt{W}} \quad (4)$$

$$\beta = \left(\frac{V_m}{R} \right) \left(\frac{\sigma}{\varepsilon^2 M} - \frac{\varepsilon_0}{D_i \sqrt{2W}} \xi(c_S^e, c_L^e) \right) \frac{m_e}{1 - k_e} \quad (5)$$

$$\xi(c_S^e, c_L^e) = \frac{R}{V_m} (c_L^e - c_S^e)^2 \times \int_0^1 \frac{(1-h(\phi))h(\phi)}{(1-h(\phi))(1-c_L^e)c_L^e + h(\phi)(1-c_S^e)c_S^e} \frac{d\phi}{(1-\phi)\phi} \quad (6)$$

where m_e is the slope of the liquidus line at equilibrium, k_e is the equilibrium partition coefficient, and D_i is the diffusion coefficient in the interface region. For the binary-alloy system, we use the same parameters shown in the literature (Ode et al.³). In addition, T is the temperature, W represents the height of the double-well potential, and V_m is the molar volume. - Equations (1) and (2) were solved numerically. They were discretized on uniform grids using an explicit finite scheme.

Anisotropy is introduced in the phase-field model as follows:

$$\varepsilon(\theta) = \varepsilon_0 \{1 + \delta_\varepsilon \cos(j \cdot (\theta - \theta_0))\} \quad (7)$$

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), θ being the angle between the direction of the phase-field gradient and the reference axis of the system.

As discussed in the preceding section, all previous phase-field model neglect or oversimplify the treatment of solute diffusion coefficient on the solid and liquid region. Usually, it is assumed as a constant during the simulation of solidification

process, as originally proposed by authors. Temperature dependence on diffusion expressed in terms of Arrhenius equation, as movement of solute through the solid and liquid regions is considered in this present paper. Mathematically, the temperature dependence of diffusion of Al-Cu alloy in liquid D_L and in solid D_S are expressed respectively as follows (Owadano^[5]):

$$D_L = 8.1 \times 10^{-7} \exp\left(-\frac{38900}{RT}\right) \quad (8)$$

$$D_S = 2.3 \times 10^{-4} \exp\left(-\frac{146000}{RT}\right) \quad (9)$$

where R express the gas constant, $8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$. Accurate knowledge of liquidus temperatures is necessary for the determination of optimum casting temperatures during casting processes. Numerous empirical equations have been derived using regression analysis to estimate the liquidus temperatures of alloys system. Due we adopt a binary system; the chemical interactions between different solutes can be neglected. For this reason, in this present paper, the equation derived from the phase diagram Al-Cu to estimate the liquidus temperature is a linear function of composition of the type:

$$T_L = -3.381. \%Cu + 660.4 \quad (10)$$

The phase-field model is used to calculate the dendrites, by imposing a constant temperature gradient in an undercooled melts system. Simulation of dendrite evolution is carried out disregarding the energy equation and instead imposing the following linear temperature profile:

$$T(t) = \Delta T - \dot{T} \quad (11)$$

where ΔT is the super-cooling level ($\Delta T = T_L - T_0$), \dot{T} is the constant value of cooling rate and T_0 is the initial temperature of binary system. In order to observe the growth of dendrites in the alloys system, the calculation must be done according to the time scale of the solute diffusion. For this reason, it was necessary to use (Ferreira et al.^[6])

$$\Delta t = \frac{\Delta x^2}{4D_i} \quad (12)$$

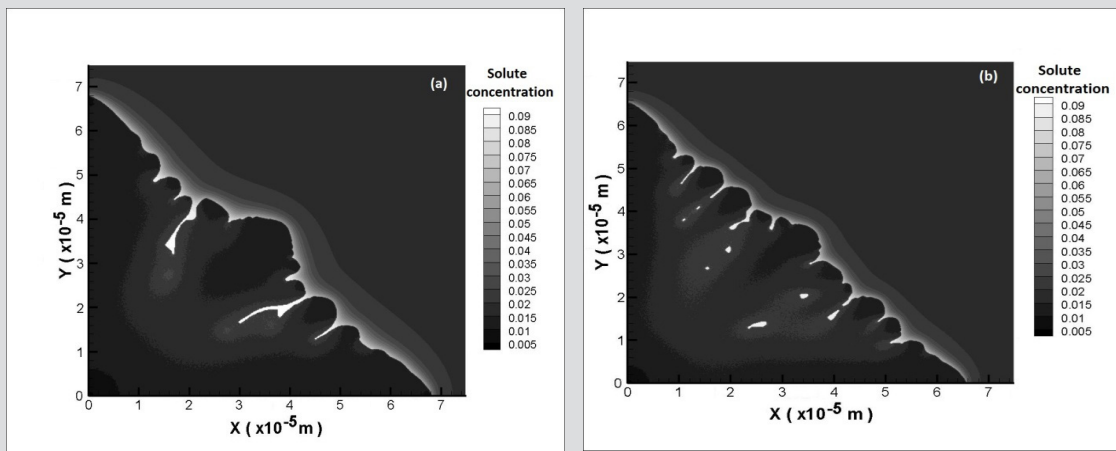


Figure 2. (a) Case I: dendrite calculated by phase-field model with Eqs. (7-9) and (b) Case II: dendrite calculated by phase-field model with both the liquidus temperature and the solute diffusivities adopted as constants.

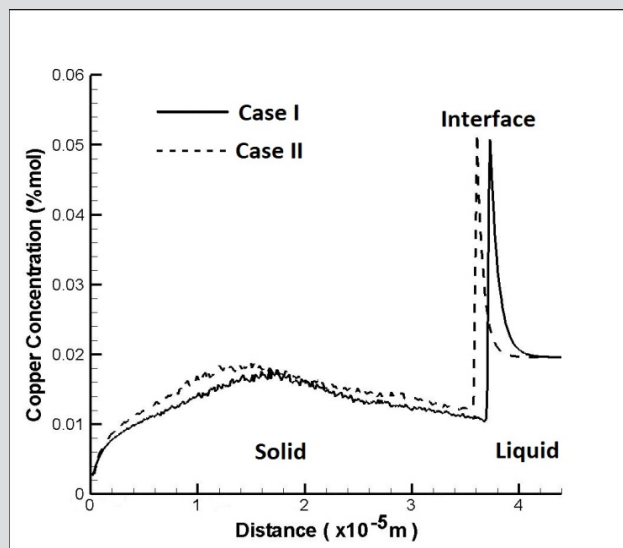


Figure 3. Copper concentration by region: solid ($\phi = +1$), liquid ($\phi = 0$) and interface ($0 < \phi < +1$).

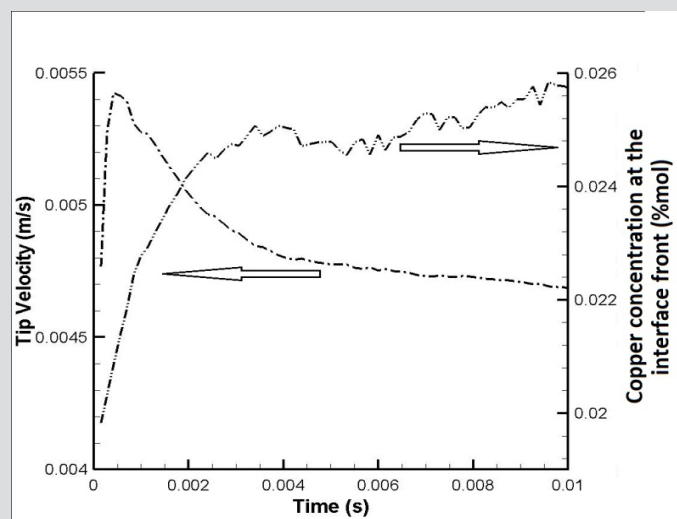


Figure 4. Velocity of dendrite tip and copper concentration versus solidification time.

Δx represents the grid spacing. The anti-symmetrical side branching from primary arms around the dendrite tip is known to be possible only with the existence of a noise source in the phase-field equation. Therefore, random noise was added to Eq. (1), in the same way as described in the work of Ferreira et al. [6]

$$\text{Noise} = 16\alpha r\phi^2(1 - \phi)^2 \quad (13)$$

where r is a randomly-generated number between +1 and -1 and α is a noise amplitude factor. From Eq. (13), the noise can be seen to reach its maximum value for $\phi = 0.5$, being null at $\phi = 0$ and $\phi = +1$.

3. Results and Discussion

The parameters and properties adopted in this study are summarized in Tables 1 and 2, respectively.

The phase-field mobility (M) in Eq. (1) is calculated by the Eqs. (5) and (6) during simulations of the solidification process. The relationships between diffusion coefficients (D_s and D_L) of Al-Cu alloy and the temperature range of interest are shown in Figure 1. These results show that a small change in temperature affects both diffusion coefficients in solid (D_s) and in liquid (D_L). One can see that results shown in Fig.1, overestimates the values adopted in previous papers. For the case of diffusivity in liquid region, the authors (Ferreira et al.^[2] and Salvino et al.^[4]) adopted a diffusivity equal to $3.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, while the values calculated are between 4.75×10^{-9} and $5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. For the diffusivity in solid region, the authors (Ferreira et al.^[2] and Salvino et al.^[4]) adopted a value of order of magnitude equal to 10^{-18} , however the diffusivities calculated are between 9.5×10^{-13} and $1.26 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$.

Taking advantage of the dendritic growth with four preferential directions ($j = 4$), only a quarter of the entire dendrite is chosen as the computational domain, and a solid seed is placed at the bottom-left corner, that is, at the origin. The equiaxed dendritic morphology and the copper concentration for Al-0.0196%molCu alloy are shown in Fig.2(a-b) at the evolution time of 0.01589 s for an initial temperature of 923K.

It can be seen that primary arm has a low concentration copper, while the liquid regions between the secondary arms have the highest concentration solute. These features are commonly found in experiments on the solidification. However, with focus on the morphology dendritic seemingly there is no great difference between the Fig. 2(a) and (b). In order to observe more details in the two dendrites shown in figure 2(a) and (b), the concentration profiles of solute in solid region and liquid is depicted in Figure 3.

Figure 3 shows the concentration profiles across of a diagonal line as obtained from the phase-field simulation (Figure 2a-b). The two different cases show concentration profiles similar. However, note that the concentration profiles are not completely horizontal, thus showing evidence of microsegregation. Also, one can see how the concentration profile obtained by phase-field simulation varies within the interface region: each curve display a sharp increase in concentration in the interface region. On each curve, the concentration profile in the solid region follows a law in the phase-field formulation, while it decays exponentially towards the initial concentration in the liquid region right after the solid/liquid interface. Still with respect to Fig. 3, both cases are characterized by same temperature gradient (G) and initial composition (C_0), but one can observe the peak concentrations in different positions during solidification process. This is due to the dendrites advance through the super-cooled liquid at different velocities. The interface velocity, in turn, it is affected by the variations of the phase-field mobility (M_0) in Eq. (5).

Figure 4 shows the velocity of dendrite tip and copper concentration versus solidification time, for the case I. At the start solidification process, one can see the high velocity of the dendrite tip, Fig.4. The tip velocity decreases quickly with the solidification time, due to a variation in phase-field mobility. This occurs due to an increase in copper concentration at the interface front and reduction of phase-field mobility. The phase-field mobility is function of copper concentration; it should be calculated with copper concentration during the computation, Eq. (5).

In order to show the applicability of the phase-field model for case I, the influence of dendrite tip radius on the interface velocity is showed.

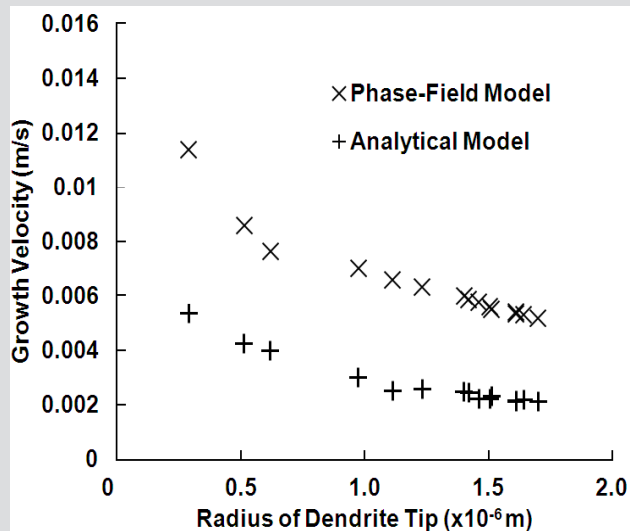


Figure 5. Growth velocity in Al-0.00196%molCu system versus radius of dendrite tip.

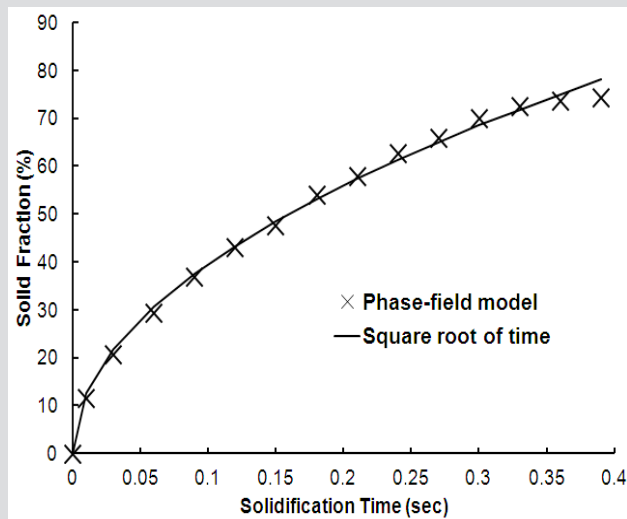


Figure 6. Solid fraction versus time.

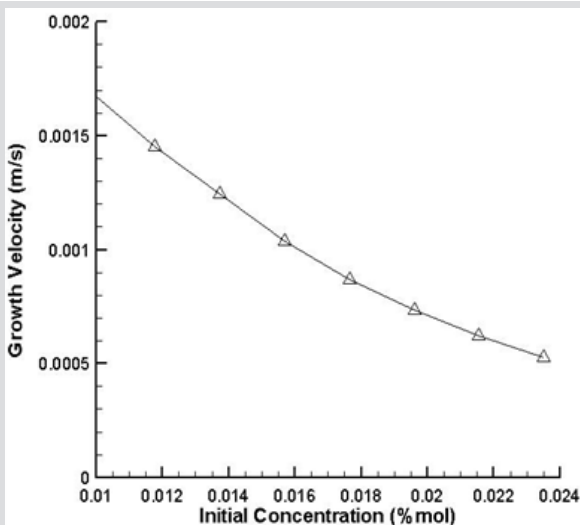


Figure 7. Growth velocity versus copper concentration.

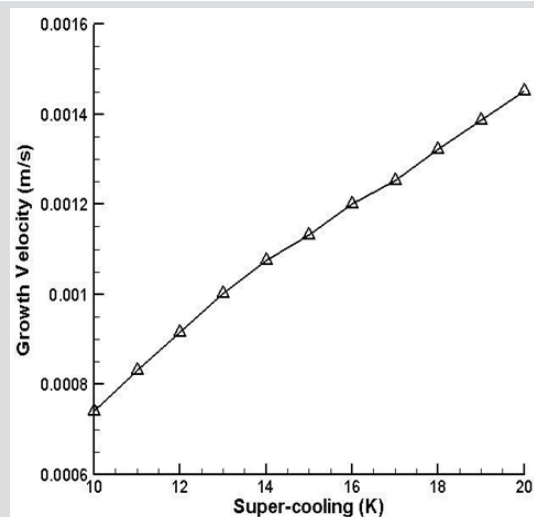


Figure 8. Growth velocity versus thermal super-cooling.

The relationships between velocity and dendrite tip radius for an Al-0.00196%molCu alloy are shown in Figure 5. Data obtained by an analytical model, proposed by Stefanescu⁷, were plotted alongside for comparison. One can see that phase-field-based results lie above those obtained by analytical model. This is due to the evolution of the solid phase (Eq. 1) is assumed to be dependent of the source term. This, in turn, depends of both concentrations in the phases and temperature.

The Stefanescu's model, on the other hand, takes into account tip radius and concentrations in the liquid region. We can see in Figure 5 that increasing the radius of dendrite tip influences the reduction of dendritic growth velocity. The numerical results for the tip velocity are consistent with experimental conclusions (Altundas and Caginalp^[8]), and compatible with literature (Stefanescu^[7]).

Figure 6 shows the evolution of solid fraction with solidification time, in this simulation, the solid fraction is given by the ratio of the solid control volume to the total volume control of the computational domain. A thin solid layer was added at the bottom boundary of the rectangular domain. In that figure, the solid fraction is seen to increase faster at the onset of solidification. This rate then gradually dwindles toward completion of the solidification process. Given that we are considering a linear temperature profile, owing to solute segregation during the change of phase, an increase of the solute concentration at the interface front occurs as consequence of the reduction of the interface mobility. Traditionally, one assumes that the solid fraction is proportional to the time or square root of the time, as any diffusion-controlled growth process (Chalmers^[9]). In the present paper, interface motion is determined by the thermodynamic force, represented by the third term in Eq. (1). Results in Figure 6 display good agreement between the calculated fraction by phase-field model and the square root of the time. But, as expected, the behavior is clearly nonlinear for binary alloy solidification (Al-0.00196%mol Cu).

The influence of copper concentration on the growth velocity is showed in Figure 7. Here, the initial concentration of system has been changed in order to evaluate the velocity at each point for

each initial concentration. The speed can be seen to decrease monotonically as copper concentration increases. This occurs because solute tends to reduce interface mobility, Eq. (5). The seeming tendency toward a linear behavior in the speed plot is a mere consequence of the short time interval considered here.

The phase-field model can be applied as a computational tool to calculate the evolution dendritic during the solidification process. In this paper, we explored the possibility to assess dependence of the velocity growth on the super-cooling, calculating the solidification of binary alloy system at different super-cooling levels from 10 to 20 K. For each transient calculation, the displacement of a dendrite tip was measured and the growth velocity of the tip of a dendrite was determined for each super-cooling level.

The results of those calculations are shown in Figure 8; the super-cooling level considered is the difference between liquidus temperature of binary alloy and initial temperature. The phase-field model predicted a linear dependence between solidification velocity and super-cooling levels, while experimental results found in the literature (Chalmers^[9]) indicate a nonlinear behavior. We surmise that the discrepancy can be explained by the fact that the linear dependence is "built into" the formulation of the phase-field model. The linear dependence on the super-cooling appears in the source term in Eq. (1), as discussed by Ferreira et al.^[10].

4. Conclusions

The phase-field model is a good tool for simulating details of dendritic morphological of binary alloy systems. The model is based on transport-like equation for the solid phase formulated in terms of a phase-variable (ϕ), which determines whether the phase is solid or liquid. In this paper, the phase-field model was applied to describe the solidification kinetics of undercooled Al-Cu binary alloy. In contrast to the others models, temperature dependence of the diffusion coefficient is considered and liquidus temperature is calculated by non-uniform concentration distribution. This approach is more physically realistic for simulation of the solidification process by phase-field model. It is important to generalize the model for include the influence of temperature and concentration. This gives a better description of

the real solidification process. The morphology dendritic calculated via phase-field model for the case I, compared to the case II, showed seemingly that there is no great difference between them (Figure 2a-b). This is because the simulations were carried out in a short period of solidification process time ($t = 0.01589$ s). Figure 3 shows the concentration profiles across of solid region, interface and liquid, calculated by phase-field model for both cases. In the two cases, the concentration profiles are similar; however, one can see the evidence of microsegregation. Here, boundary and initial conditions are the same for two cases, except for diffusivity and liquidus temperature. One can see, the interface of the Case I, is further displaced to the right in Fig. 3. It indicates that interface velocity is higher in this condition. The velocity of dendrite tip and solute concentration were calculated for the case I. The velocity is high, while copper concentration is low at the onset solidification process. In the Figure 4, the concentration is seen to increase faster at the onset of solidification process. This rate then gradually dwindles toward completion of the solidification process. Changes in copper concentration, in turn, affect the velocity of dendrite tip. The growth velocity versus radius of dendrite tip is analyzed and compared with analytical model. The profile calculated for growth velocity by phase-field model show reasonable agreement with those from the Stefanescu's equation. For one-dimensional numerical simulations, the calculation results show good agreement with the solidification theory. That is, the solid fraction is roughly proportional to the square root of the time lapsed, Figure 6. Changes in initial concentration of system affect the growth velocity, Figure 7. This effect lowers the interface velocity, which, in turn, requires a longer time to solidify. Finally, an appreciable increase of the velocity growth occurs as a consequence of the increase of the super-cooling, Figure 8, which is due to the fact that the super-cooling considered is the difference in temperature between liquidus and the initial liquid.

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