

The effect of excess energy in the simulation of dendritic growth using the phase field model coupled with a CALPHAD database.

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Abstract

In this work, we aim to use the Warren-Boettinger model for isothermal solidification to predict the dendritic growth in binary alloys; using the phase field method coupled with a CALPHAD database (CALCulation of PHase Diagram). The main benefit of this work is to study the effect of the excess energy in the phenomena of dendritic growth for the real solution. We took in consideration, the contribution of the regular solution interaction parameter associated with the excess energy of mixing solid and liquid in the phase field equation $\varphi(x, t)$ and the concentration equation $c(x, t)$. The model we proposed is able to simulate the microstructural evolution of the real solution Ni-Cu by linking directly the phase field model to the CALPHAD thermodynamic database. The comparison of the numerical calculations for the Ni-Cu real solution and the Ni-Cu ideal solution shows that the addition of the excess energy has an important effect on the dendrite form.

Keywords: *Dendritic growth; Phase field model; CALPHAD; Excess energy.*

1. Introduction

The phase field models have become an important tool in material science simulation [1], i.e : the formation of microstructure and growth of dendrites [2] and the process of solidification of binary alloys [3-7]. They have been the subject of numerous studies and different simulation [8]. The phase field method is a powerful kinetic tool for simulating microstructure evolution at the meso-scale [9-12], whereas phase equilibrium information such as equilibrium phases and their compositions can be obtained from the CALPHAD method [13-17]. Therefore, the coupling of these two methods is useful for effectively predicting kinetic microstructure evolution in alloy systems. The phase field simulation coupled with the CALPHAD method have also been reported for solidification such as temporal evolution of interfacial composition profiles during solidification, dendrite growth, and solidification microstructure formation [18- 24].

The numerical simulation adopted and performed in this work for the dendritic growth in the case of binary alloy was much discussed previously, for example we mention in this context the work of Warner and Boettinger [6], who created the first model to predict the dendritic growth in binary alloys, Steinbach [25,26], Provatas and Elder [27], Chen [28], and in particularly the work of Mathis Plapp [29], they studied the digital side by changing the methods of solving and mesh pattern. All these works treated the Ni-Cu alloys as an ideal solution where the mixing energy is neglected. For example the

model of Warner and Boettinger [6] imposes an ideal Ni-Cu solution, but indeed, considering the Ni-Cu solution as ideal is not entirely justified, since in reality it may not be close to the ideal, despite the similarity of the physical properties of Ni and Cu elements and the nature of the Ni-Cu phase diagram [27].

In a real solution AB, it is necessary that the energy of the mixture called also the excess energy is less than the energy of pure elements A and B (for more details see ref [31]). Our contribution falls within this context; it involves the development of the Warner and Boettinger model [6], where we consider the Ni-Cu alloy as a real solution by introducing the term of excess energy. To get this contribution, we must take into account the interaction parameter associated with the excess energy of mixing solid and liquid phases [6, 30, 31]. The thermodynamic modeling of the Ni-Cu phase diagram with CALPHAD methods gives us directly the excess energy parameters of solid and liquid phases. This setting was previously assumed to be zero in the model of Warner and Boettinger [6] also the same in [7, 9, 27]. The introduction of the interaction parameter in the phase field and the concentration equations in the model of Warner and Boettinger lead us finally to a model reflecting dendritic growth for real solutions.

Our contribution is to study the dendritic growth of a real solution, the growth evolution is presented and a comparative study is made between our results and the others results found in the literatures.

2. Mathematical Model

The Warren-Boettinger model [6] describes the progress of solidification of binary alloy in time t , by two partial differential equations system, the phase field and the concentration equations with two independent variables: φ and concentration, c .

2.1. The phase field equation

$$\frac{1}{M_\varphi} \frac{D\varphi(x,t)}{Dt} = \bar{\epsilon}^2 \nabla \cdot (\eta^2 \nabla \varphi) - (1-c)H_A(\varphi, T) - cH_B(\varphi, T) - \bar{\epsilon}^2 \frac{\partial}{\partial x} \left(\eta \eta' \frac{\partial \varphi}{\partial y} \right) + \bar{\epsilon}^2 \frac{\partial}{\partial y} \left(\eta \eta' \frac{\partial \varphi}{\partial x} \right) \quad (1)$$

Where:

$M_\varphi > 0$: is the interfacial mobility

$$M_\varphi = cM_B - (1-c)M_A \quad (2)$$

$$M_X = \frac{(T_m^X)^2 \beta_X}{\sqrt{2} L_X \delta_X} \quad (3)$$

β_X The linear kinetic coefficient of component X ,

T_m^X The melting temperature of component X ,

δ_X The interface thickness of component X ,

L_X The latent heat of component X

$$\bar{\epsilon}^2 = \frac{6\sqrt{2}\delta_X\sigma_X}{T_m^X} \quad (4)$$

σ_X The surface energy of component X

H_X The free energy of element X

$$H_X(\varphi, T) = W_X g'(\varphi) + 30g(\varphi)L_A \left(1 - \frac{T}{T_m^X}\right) \quad (5)$$

T The absolute temperature

$$g(\varphi) = \varphi^2(1-\varphi)^2 \quad (6)$$

$$g'(\varphi) = \frac{\partial g(\varphi)}{\partial \varphi} \quad (7)$$

$$W_X = \frac{3\sigma_X}{\sqrt{2}T_m^X\delta_X} \quad (8)$$

In order to include the effects of anisotropy η in the model, Warner and Boettinger [6] follow the ideas put forth by [2, 4] and [24]:

$$\epsilon_\theta = \bar{\epsilon}\eta = \bar{\epsilon}(1 + \gamma \cos k\theta) \quad (9)$$

Where θ is given by equation:

$$\tan\theta = \frac{\varphi_y}{\varphi_x} \quad (10)$$

φ_x, φ_y : are the partial derivatives of φ .

$$\eta' = \frac{\partial \eta}{\partial \varphi} \quad (11)$$

γ : The anisotropy

k : The mode number

2.2. The concentration equation

$$\frac{Dc}{Dt} = \text{div} \left(D(\varphi) \left(\nabla c + \frac{V_m c(1-c)}{R} (H_B(\varphi, T) - H_A(\varphi, T)) \nabla \varphi \right) \right) \quad (12)$$

$D(\varphi)$ The inter diffusion coefficient

$$D(\varphi) = D_s + p(\varphi)(D_L - D_s) \quad (13)$$

D_L, D_s The diffusivities in liquid and solid respectively

$$p(\varphi) = \varphi^3(10 - 15\varphi + 6\varphi^2) \quad (14)$$

V_m : The specific volume

R : The gas constant

2.3. The addition of excess energy term in the model

In the warren-Boettinger model [6], the Ni-Cu is an ideal solution, so the interaction parameter $\lambda(\varphi) = 0$, but in our prediction $\lambda(\varphi)$ is associated with the excess energy of mixing solid and liquid [30, 31] and equal to:

$$\lambda(\varphi) = \lambda_s + p(\varphi)(\lambda_L - \lambda_s) \quad (15)$$

λ_s, λ_L : The excess energy of mixing solid and liquid respectively.

$$\text{And, } \frac{\partial \lambda(\varphi)}{\partial \varphi} = p(\varphi)'(\lambda_L - \lambda_s) \quad (16)$$

λ_S, λ_L : They are presented by the Redlich-Kister polynomial [30] in the thermodynamic assessment of the binary systems by CALPHAD methods. These energies are given by: [30, 31]

$$\lambda_S = \sum_{i=0}^n (a_i^S - b_i^S T)(1 - 2c)^i \quad (17)$$

$$\lambda_L = \sum_{i=0}^n (a_i^L - b_i^L T)(1 - 2c)^i \quad (18)$$

Where: $(a_i^S, b_i^S), (a_i^L, b_i^L)$ are the interactions parameters between the atoms in solid and liquid respectively. These parameters can be taken directly from the development of the phase diagram using the CALPHAD method. If $i = 0$ the solution is regular else the solution is real.

After replacing $\lambda(\varphi)$ in the phase field development, we find the new free energies:

$$H_A^E(\varphi, T) = W_A g'(\varphi) + L_A p'(\varphi) \left(1 - \frac{T}{T_m^I}\right) + \frac{c^2}{T} [30g(\varphi)[(a_i^L - b_i^L T)(1 - 2c)^i - (a_i^S - b_i^S T)(1 - 2c)^i] \quad (19)$$

$$H_B^E(\varphi, T) = W_B g'(\varphi) + L_B p'(\varphi) \left(1 - \frac{T}{T_m^I}\right) + \frac{(1 - c)^2}{T} [30g(\varphi)[(a_i^L - b_i^L T)(1 - 2c)^i - (a_i^S - b_i^S T)(1 - 2c)^i] \quad (20)$$

Finally the phase field and concentration equations for the real solution with the excess energy addition are:

$$\frac{1}{M_\varphi} \frac{D\varphi(x, t)}{Dt} = \bar{\epsilon}^2 \nabla \cdot (\eta^2 \nabla \varphi) - (1 - c) H_A^E(\varphi, T) - c H_B^E(\varphi, T) - \bar{\epsilon}^2 \frac{\partial}{\partial x} \left(\eta \eta' \frac{\partial \varphi}{\partial y} \right) + \bar{\epsilon}^2 \frac{\partial}{\partial y} \left(\eta \eta' \frac{\partial \varphi}{\partial x} \right) \quad (21)$$

$$\frac{Dc}{Dt} = \text{div} \left(D(\varphi) \left(\nabla c + \frac{V_m c (1 - c)}{R} (H_B^E(\varphi, T) - H_A^E(\varphi, T)) \nabla \varphi \right) \right) \quad (22)$$

3. Computer Program : Numerical simulation

We present physical simulation of the dendrite growth during the solidification of Ni-Cu alloy. To perform this

simulation, we consider the two dimensional isothermal anisotropic model of Warren and Boettinger [6] with the introduction of the excess energy in the model. As we know, in the phase field models, the interface thickness between the solid and liquid interfaces must be very small, this restriction requires a very dense mesh in the simulations of dendrite growth such that the mesh size should be sufficiently less than the interface thickness, otherwise the simulation of dendritic growth cannot be realized [7]. The model was solved with boundary conditions applied only at the edges of a computational box. Zero Neumann boundary conditions for c and φ were imposed at the boundaries. The phase field and concentration equations are solved on two dimensional uniform grids with the grid spacing $\Delta x, \Delta y$ using finite difference approximations to the derivatives, the second order for space discretization and the first order centered difference formula for time discretization. The choice of the numerical method to solve the equation φ and c influences only over the time of resolution, not the results

For convenience, the governing equations (21) and (22) are transformed into dimensionless form. Length and time have been scaled with a reference length $l = 0.94 \delta$ and the diffusion time $\frac{l^2}{dl}$ respectively [6,7]. The dimensionless form of discretization is:

$$\frac{\varphi^{t+1} - \varphi^t}{\Delta t} = \varepsilon_2 \left[\eta^2 \Delta \varphi^t - (1 - c^t) \frac{l^2 H_a^E}{\varepsilon^2} - c^t \frac{l^2 H_b^E}{\varepsilon^2} \right] + \varepsilon_2 \eta \eta' [\sin(2\theta) (\overline{\varphi_{yy}^t} - \overline{\varphi_{xx}^t}) + \overline{\varphi_{xy}^t} 2 \cos(2\theta)] - \frac{\varepsilon_2}{2} (\eta'^2 + \eta \eta'') [2 \sin(2\theta) \overline{\varphi_{xy}^t} - \Delta \varphi^t - \cos(2\theta) (\overline{\varphi_{yy}^t} - \overline{\varphi_{xx}^t})] \quad (23)$$

$$\frac{c^{t+1} - c^t}{\Delta t} = \bar{d} \Delta c^t + \bar{d} c^t (1 - c^t) \left(\frac{V_m}{R} H_b^E - \frac{V_m}{R} H_a^E \right) \Delta \varphi^t + [\bar{d} p + \bar{d} (1 - 2c^t) \left(\frac{V_m}{R} H_b^E - \frac{V_m}{R} H_a^E \right)] \Delta \varphi^t \Delta c^t + c^t (1 - c^t) [\bar{d} p \left(\frac{V_m}{R} H_b^E - \frac{V_m}{R} H_a^E \right) + \bar{d} \left(\frac{V_m}{R} H_b^E p - \frac{V_m}{R} H_a^E p \right)] \Delta \varphi^t \Delta \varphi^t \quad (24)$$

$$dl = D_l [m^2/s] \quad (25)$$

$$\varepsilon_2 = \frac{M_\varphi \bar{\epsilon}^2}{dl} \quad (26)$$

$$l = 0.94 \delta [m] \quad (27)$$

$$\Delta x = \frac{\Delta x}{l} \quad (28)$$

$$\Delta t = \frac{\Delta t dl}{l^2} \quad (29)$$

$$\bar{d} = \frac{d}{dl} \quad (30)$$

$$\frac{dp}{dl} = \frac{dp}{dl} \quad (31)$$

$$dp = \frac{\partial p}{\partial \varphi} \quad (32)$$

$$H_b^E p = \frac{dH_b^E p}{d\varphi} \quad (33)$$

$$H_a^E p = \frac{dH_a^E p}{d\varphi} \quad (34)$$

4. Results and Discussion

We have developed a computer program to simulate the progress of dendritic growth using the finite difference method for solving the governing differential equations system (phase field and concentration). The simulation conditions of dendrite solidification process have a significant effect on the simulated microstructure. In this simulation, the calculation of the solidification progress is carried out using a square box size of 35 μm with grid point numbers 750x750. The initial condition was a small square area of solid $\varphi = 0$ in the center of a liquid $\varphi = 1$ with the concentration everywhere equals c_0 . We have used the physical data of Ni-Cu real solution (see table1) where the alloy containing $c_0 = 0.408$ atomic fraction of Cu in Ni and $T=1574$ K. For this temperature, the equilibrium concentration is in the liquid $c_l = 0.4668$ and in the solid $c_s = 0.3994$. Therefore, the initial super-saturation of liquid was $\Delta = 0.86$. For the interaction parameters, they are calculated by Miettinen [31], where the excess enthalpies of solid and liquid phases are developed to the first order ($a_0^S = 8366$, $b_0^S = 2.802$, $a_0^L = 11760$, $b_0^L = 1.084$, $a_1^S = -4360$, $b_1^S = 1.812$, $a_1^L = -1670$, $b_1^L = 0$) in the thermodynamic assessment of (Ni-Cu-Sn) system by CALPHAD method and Redlikh-Kister model.

Table1. Physical data of Cu and Ni elements [10].

Propriety	Unit	Nickel	Cooper
Melting temperature (T_m)	K	1728	1358
Latent heat (L)	J/m^3	2350.10^6	1758.10^6
Diff. coef. liquid (D_l)	m^2/s	10^{-9}	10^{-9}
Diff. coef. solid (D_s)	m^2/s	10^{-13}	10^{-13}
Linear kinetic coefficient (β)	$m/K/s$	$3.3 \cdot 10^{-3}$	$3.9 \cdot 10^{-3}$
Interface thickness (δ)	m	$8.48 \cdot 10^{-8}$	$6.01 \cdot 10^{-8}$
Surface energy (σ)	J/m^2	0.37	0.29
Molar volume (V_m)	m^3	$7.46 \cdot 10^{-6}$	$7.46 \cdot 10^{-6}$
Mode Number (k)		4	4
Anisotropy (γ)		0.04	0.04

5. Results

The figures (1.a, 1.b, 1.c and 1.d) show the microstructure development for the case of Ni-Cu real solution where the excess energy is well-considered. The figure (1.a) presents the initial solid seed where ($\varphi = 0$). The figures (1.b, 1.c, and 1.d) show that the value of the phase field parameter φ decreases from 1 to 0; this means a variation in the solid concentration, therefore, the initial seed grows. On the other hand, we see the appearance of primary branches of the dendrite and also the creation of second branches between the primary ones. In the figure (1.d) we remark an overlap of the primary and second branches. Figure (1.e) presents the variation of φ in function of time (t), as can be seen, the variation of the order parameter φ is almost linear, where it decreases rapidly until zero, which represents the time of dendritic formation and, $\Delta t = 1.11$ represent the time of formation.

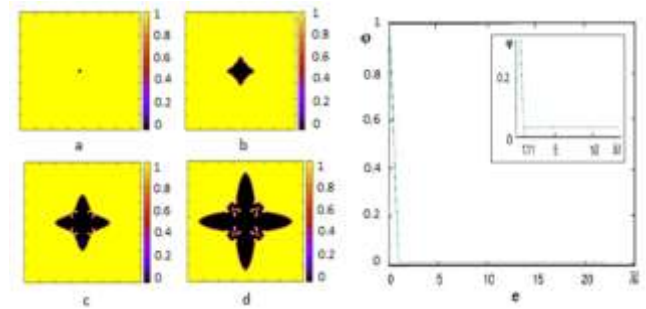


Fig.1 Dendritic growth with excess energy at different time t (a, b, c, and d: φ distribution, e: φ variation).

The figures (2.a, 2.b, 2.c and 2.d) show the concentration distribution at different time (t). The figure (2.a) presents the initial solution containing $c_0=0.408$ atomic fraction of Cu in Cu-Ni alloy. The figure (2.e) shows that the value of the concentration of Cu element in the area of the dendrite changes in the range [0.39, 0.47], the concentration of Cu increases from 0.408 to 0.425 almost linearly, then it decreases from 0.425 to 0.408 with a slope shape. The increases phase corresponds to the formation of the dendrite shape, and the decreases phase presents the rejecting of Cu element. In the previous pictures, we remark the creation of a thin film rich in Ni around the shape of the dendrite, due to the absorption of Cu element by the dendrite from the interface liquid-solid. According to figures (2.e), the variation of c proves also the

complete formation of the dendrite at $\bar{\Delta}t = 1.11$ as can be seen in figure (1.e).

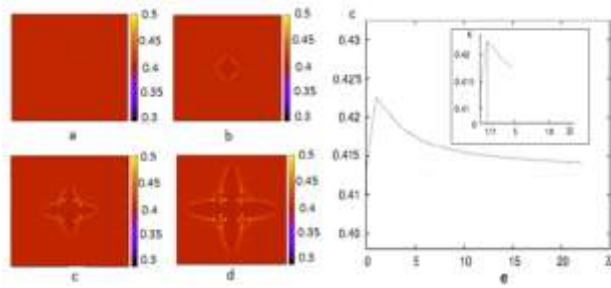


Fig. 2 Dendritic growth with excess energy at different time t (a, b, c, and d: concentration distribution, e: concentration variation).

Figure 3 shows the phase field distribution of the dendritic growth simulation, using the Warren-Boettinger model [6] by Adrian et al. Ref [9], where they have treated the effect of the noise term in figure 3.a and 3.b. Also, figure 3.c shows the phase field distribution where we have added the effect of excess energy.

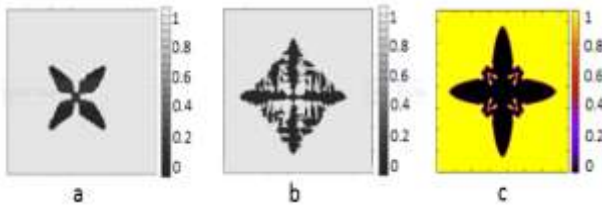


Fig. 3 The results of simulation of dendritic growth of ϕ distribution (a: without noise term [9], b: with noise term [9], c: our work without noise).

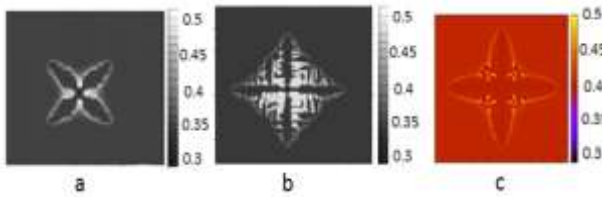


Fig. 4 The results of simulation of dendritic growth of c distribution (a: without noise term [9], b: with noise term [9], c: our work without noise).

The calculation of dendrite growth with neglecting the noise term and the effect of excess energy gives the dendrite a shape of a four simple clover leaves (see figure 3.a). The introduction of the excess energy factor to the phase field and concentration equations changes the dendrite form. Numerical calculations show that the introduction of the excess energy in the model of Warren

and Boettinger [6] produce the second branch without the addition of the noise term and also a secondary branches grow between the axis of principal branches (see figure 3.c).

The comparison between our results and the results of Adrian et al. Ref. [9] shows clearly a difference between the Ni-Cu ideal solution and Ni-Cu real solution growth behavior. This latter drives us to conclude that the effect of the introduction of the excess energy gives to the dendrite a second branches between the principal ones, even if there is no noise term.

In the modeling of Ni-Cu ideal solution, the dendrite shape does not change after the formation of the principal branches. But in the modeling of dendritic growth of Ni-Cu real solution, we see the formation of the second branches between the principal ones, then an overlap of the primary and second branches.

6. Conclusions

- The model of Warner and Boettinger is limited to modeling the ideal solution, but the changes we have made to this model has improved it to model the dendritic growth whatever the nature of its solution.
- the development of Warner and Boettinger model by adding the excess energy, gives us an attempt to find out the effect of this energy in dendritic growth
- We have not studied the noise effect with the excess energy effect at the same time, because the two effects produce side branches so we can't distinguish the difference between them.
- The simulation of the simple case of dendritic growth (neglecting excess energy and the noise term) presents a simple leaves has four branches but:

- The addition of excess energy produces inter-branches which grow between the principal branches with an angle of 45° .
- The addition of the noise produces branches perpendicular to the principal branches.

So the difference between the two previous additions can be a subject of discussion to future research.

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