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## Phase-Field Modelling of Zinc Dendrite Growth in ZnAlMg Coatings

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In the present work, a phase-field model for dendritic solidification is applied to hot-dip ZnAlMg coatings to elucidate the morphology of zinc dendrites and the solute segregation leading to the formation of eutectics. These aspects define the microstructure that conditions the corrosion resistance and the mechanical behaviour of the coating. Along with modelling phase transformation and solute diffusion, the implemented model is partially coupled with the tracking of crystal orientation in solid grains, thus allowing the effects of surface tension anisotropy to be considered in multi-dendrite simulations. For this purpose, the composition of a hot-dip ZnAlMg coating is assimilated to a dilute pseudo-binary system. 1D and 2D simulations of isothermal solidification are performed in a finite element solver by introducing nuclei as initial conditions. The results are qualitatively consistent with existing analytical solutions for growth velocity and concentration profiles, but the spatial domain of the simulations is limited by the required mesh refinement.

**Keywords:** ZnAlMg coatings, Dendritic solidification, Phase-field model, Crystal orientation

### 1. Introduction

Corrosion protection is often a major requirement of steel structures and, traditionally, zinc-rich metallic coatings have been used to cover steel sheets to this effect. In fact, zinc provides galvanic protection to the steel substrate. This protection must be combined with an appropriate mechanical behaviour, so that corrosion do not reach steel by coating decohesion or cracking. Consequently, the balance between anticorrosive and mechanical properties, as well as other factors such as lightweighting and cost reduction, condition the optimisation approaches of these coatings. In this sense, ZnAlMg coatings have created great interest in industry.

#### 1.1 ZnAlMg coatings

Provided that the additions of aluminium and magnesium do not change the primary phase to be other than zinc, the microstructure of ZnAlMg coatings is composed of zinc dendrites surrounded by binary and ternary eutectics [1,2]. The main contributions of adding

aluminium to the zinc bath are its inherent passivation [3], and the formation of Fe-Al or Fe-Al-Zn intermetallic compounds at the substrate-coating interface, instead of brittle layers of Fe-Zn intermetallic compounds [4,5]. As for magnesium additions, corrosion resistance is improved because anodic reactions happen preferentially in phases containing this element and its corrosion products are especially protective [6-8]. Nonetheless, the influences of these and other alloying elements in mechanical behaviour and corrosion are not thoroughly understood, which is necessary to set the relations between microstructure and in-service response.

Regarding corrosion aspects, Osório *et al.* concluded that there are three key factors in zinc-rich coatings [6]: the elements in the alloy, their electrochemical behaviour and the solidification cooling rate. The latter can alter the phase fractions in the microstructure and, more importantly, high cooling rates promote the nucleation of primary dendrites resulting in finer microstructures with more atoms in solution. In general, finer microstructures are considered to be less corrosion resistant, since grain boundaries act as corrosion initiation sites due to the presence of defects, plastic deformation and segregated

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impurities [6,9-11]. Nevertheless, Osório *et al.* found that the secondary dendrite arm spacing and the hypoeutectic or hypereutectic nature of ZnAl alloys play also a major role in corrosion resistance [6].

Similarly, it has often been observed that magnesium prevents intergranular corrosion despite making microstructure finer [8,12,13]. In fact, magnesium has a more negative electrode potential than zinc and aluminium ( $E_{Mg} < E_{Zn} < E_{Al}$ ), so a fine microstructure facilitates the precipitation of its corrosion products in cathodic phases. This helps to keep acidity more uniform all over the surface and micro-galvanic coupling between different phases is also reduced [8], which results in a less intense and more uniform corrosion attack. Nonetheless, the values of electrode potentials can be inversed depending on environmental conditions such as acidity and temperature. For example, Prosek *et al.* observed that aluminium phases activate and dissolve before zinc in alkaline environments for Zn5.1Al (wt%) [8]. These studies demonstrate that phase fractions, their morphologies and solute distributions condition the corrosion behaviour of ZnAlMg microstructures, with the alloying elements and the solidification process being decisive factors. The same holds for the mechanical behaviour of these coatings, given the diversity of microconstituents and their different properties [1,2,9].

## 1.2 Phase-field modelling of dendritic growth

Phase-field models are known to be efficient in solving solidification problems, by representing that the liquid-solid transformation occurs continuously across an interface of finite thickness [14]. This method offers the possibility to simulate solidification morphologies and, when it is coupled with diffusion equations, solute concentration fields are also obtained. According to the previous section, this information and thus phase-field models are of great interest to understand and predict the microstructures of zinc-rich coatings, as well as their mechanical and corrosion properties. In particular, a model for isothermal dendritic solidification of dilute binary alloys proposed by Karma *et al.* has been extensively developed since the 1990s [15-17]. The main advantage of this formulation is the decoupling of bulk and interfacial energies in equilibrium, by considering the equality of chemical potentials on both sides of the

solid-liquid interface [18] and by assuming linear liquidus and solidus. Results of numerical simulations for various materials can be found in literature [19,20]. As for ZnAlMg coatings, Kim *et al.* studied the morphology of zinc dendrites in Zn0.2Al coatings by considering three preferential growth directions ( $\langle 10\bar{1}0 \rangle$ ,  $\langle 0001 \rangle$  and the directions normal to the  $\{12\bar{1}1\}$  planes) [21]. Regarding multiphase multicomponent models, De Bruycker *et al.* simulated Zn5Al and Zn4Al2Mg microstructures [22] and Mogeritsch *et al.* carried out simulations for Zn2.5Al1.5Mg [23]. Aiming at large scale multi-dendrite simulations, adaptive meshing [24] and non-linearly preconditioned formulations [25] have been applied to reduce the computational cost. Several proposals for tracking the crystal orientation can also be found: local front tracking [25,26], and variations of the KWC model [27,28] with different formulations of the orientational energy [29,30].

The aim of this study is to develop a phase-field model for hot-dip ZnAlMg coatings, focusing on the simulation of multiple primary zinc dendrites. Given that this family of coatings often exhibits a pronounced basal texture and that dendrite branches typically span the entire thickness of the coating [12,31], the main simulations presented in this study are 2D simulations in a plane parallel to the substrate-coating interface, with the c-axis of the hexagonal close-packed (HCP) lattice oriented perpendicular to the simulation plane. Only  $\langle 10\bar{1}0 \rangle$  directions are therefore considered as preferential growth directions, which implies 6-fold dendrites. The phase-field model adopted is that developed by Karma *et al.* [15,16], so the ZnAlMg system is treated as a pseudo-binary system where the alloying elements are considered as a unique chemical species. The tracking of crystal orientation is done by adopting the energy formulation of Henry *et al.* [29] and implementing a partial coupling with the phase-field equations. The composition of the coating used in the simulations is Zn4.67Al0.43Mg.

## 2. Phase-field Modelling

### 2.1 Phase-field and diffusion equations

The model proposed by Karma *et al.* [15,16] deals with the dendritic solidification of binary alloys, where

two variables are considered: the order parameter  $\phi$  and the solute concentration  $c$ . The former varies between -1 and 1, which correspond to the values in the liquid and solid bulk, respectively. The latter varies between 0 and 1, and corresponds to the atomic fraction of solute. Both variables are dimensionless. Temperature  $T$  could also be considered as a variable by adding the corresponding thermal diffusion equation [17], but temperature is considered as an externally imposed constant parameter in this study concerning isothermal solidification.

The first step to build the phase-field model is the formulation of the free energy functional  $F$ , which is often represented as follows (A refers to the main element and B to the solute elements):

$$\begin{aligned} F(\phi, \nabla \phi, c, T) &= \int_V f(\phi, \nabla \phi, c, T) dV \\ &= \int_V \left[ \frac{\sigma}{2} \|\nabla \phi\|^2 + f_H(\phi) + f_{AB}(\phi, c, T) \right] dV \end{aligned} \quad (1)$$

The first two terms of the integral in equation (1) correspond to the interfacial energy and the third one corresponds to the bulk energy. The bulk energy of each phase ( $f_L$  for liquid and  $f_S$  for solid) can be obtained from thermodynamic databases, and in this model its value depends on  $c$  and  $T$ . When there are several phases in the system, the bulk energy of the system also depends on the phase fractions, so in the case of solidification,  $f_{AB}(\phi, c, T)$ . Regarding interfacial energy,  $f_H(\phi)$  corresponds to a double-well potential that links the bulk energies of the liquid and solid phases, by ensuring that equilibrium can be reached in both phases. For example,  $f_H(\phi) = H(-\phi^2/2 + \phi^4/4)$ , where  $H$  is the height of the energy barrier between the two phases. The phase-field gradient term  $\sigma \|\nabla \phi\|^2/2$  in equation (1) is a penalty factor for the transition between phases to ensure a finite interface thickness, where  $\sigma$  is a coefficient in which anisotropy aspects can be introduced.

In the case of a dilute binary alloy, the following expression can be deduced for the free energy density of the system by assuming linear liquidus and solidus curves, and equal chemical potentials on both sides of the solid-liquid interface [14,16]:

$$\begin{aligned} f(\phi, \nabla \phi, c, T) &= \frac{3W\gamma}{4\sqrt{2}} \|\nabla \phi\|^2 + \frac{3\gamma}{2\sqrt{2}W} \left( \frac{-\phi^2}{2} + \frac{\phi^4}{4} \right) + f_{LA}(T_{mA}) \\ &\quad - (T - T_{mA}) \left\{ s_{LA} - \frac{L_A}{2T_{mA}} \left[ 1 + \frac{15}{8} \left( \phi - \frac{2\phi^3}{3} + \frac{\phi^5}{5} \right) \right] \right\} \\ &\quad + c(T_{mB} - T_{mA}) \left\{ s_{LB} \right. \\ &\quad \left. - \frac{L_B}{T_{mB} \ln(k)} \ln \left[ \frac{1}{2} + \frac{k}{2} - \frac{15}{16} \left( \phi - \frac{2\phi^3}{3} + \frac{\phi^5}{5} \right) (1-k) \right] \right\} \\ &\quad + \frac{RT_{mA}\rho}{P} [c \ln(c) - c] \end{aligned} \quad (2)$$

where  $W$  is a length proportional to the interface thickness,  $\gamma$  is the interfacial energy,  $T_{mi}$  is the melting point of the chemical element  $i$ ,  $f_{LA}$  is the bulk free energy density of A in the liquid phase,  $s_{Li}$  is the entropy value of  $i$  in the liquid phase,  $L_i$  is the latent heat of  $i$ ,  $\rho$  is the mass density,  $P$  is the molar mass,  $R$  is the ideal gas constant, and  $k$  is the partition coefficient which is the ratio between the equilibrium solute concentrations in the solid and liquid phases ( $c_{s0}/c_{l0}$ ). Under equilibrium conditions, the evaluation of interfacial energy yields into  $\gamma = IWH$  where  $I = 2\sqrt{2}/3$ .

The next step is to develop the evolution equations of  $\phi$  and  $c$ . The non-conserved variable  $\phi$  evolves with the time-dependent Ginzburg-Landau equation (3), whereas the conserved variable  $c$  is governed by the mass balance equation of solute (4):

$$\frac{\partial \phi}{\partial t} = -Q \frac{\delta F(\phi, \nabla \phi, c)}{\delta \phi} \quad (3)$$

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[ M(\phi, c) \nabla \frac{\partial F(\phi, \nabla \phi, c)}{\partial c} \right] \quad (4)$$

where  $Q$  is the kinetic constant and  $M(\phi, c)$  is the mobility of solute. Crystal anisotropy is introduced in the interfacial energy [32] and, since  $\nabla \phi / \|\nabla \phi\|$  is the normal unit vector of the solid-liquid interface, surface tension anisotropy can be introduced by considering  $\gamma(\nabla \phi)$ , with the most common option being to consider  $W(\nabla \phi)$  and keep  $H$  isotropic [32]. The anisotropy of attachment kinetics is not considered in this study [31], because a 6-fold symmetry is enough to consider only  $\langle 10\bar{1}0 \rangle$  directions as preferential:

$$\begin{aligned} W(\nabla \phi) &= W_0 [1 + \varepsilon_c \cos(6\alpha)] \\ &= W_0 [1 + \varepsilon_c (2n_x^6 - 12n_x^4 n_y^2 + 18n_x^4 n_y^2 - 1)] \end{aligned} \quad (5)$$

where  $W_0$  is the isotropic “interface thickness”,  $\varepsilon_c$  is the anisotropy coefficient,  $n_i = \varphi_i' / \|\nabla \varphi\|$  are the components of the normal unit vector of the solid-liquid interface expressed in terms of the gradient and partial derivatives of  $\varphi$  with respect to X- and Y-axes, and  $\alpha = \arctan(\varphi_y' / \varphi_x')$  is the angle between this normal unit vector and the X-axis, by assuming that 2D simulations are done in the X-Y plane. The combination of equations (1), (3) and (4) leads to the following evolution equation:

$$0 = -\tau \frac{\partial \varphi}{\partial t} + \nabla \cdot \left[ W(\nabla \varphi) \|\nabla \varphi\|^2 \frac{\partial W(\nabla \varphi)}{\partial \nabla \varphi} + W^2(\nabla \varphi) \nabla \varphi \right] + \varphi - \varphi^3 - \frac{\lambda}{1-k} \left[ \frac{c}{c_0(\varphi)} - 1 \right] (1 - \varphi^2)^2 \quad (6)$$

where  $\tau = 1/(QH)$  is the phase-field relaxation time,  $\lambda$  is the interface-bulk coupling parameter and  $c_0(\varphi)$  is the equilibrium concentration profile.

$$\lambda = \frac{15RT_{mA}(1-k)^2 c_{L0} \rho}{16HP} \quad (7)$$

$$c_0(\varphi) = \frac{c_{S0} + c_{L0}}{2} + \varphi \frac{c_{S0} - c_{L0}}{2} \quad (8)$$

$$c_{S0} = k c_{L0} = k \left( c_{nom} + \frac{T_{liquidus} - T}{|m|} \right) \quad (9)$$

where  $m$  is the slope of the liquidus,  $c_{nom}$  is the nominal solute concentration of the coating and  $T_{liquidus}$  is its liquidus temperature. As for the evolution of  $c$ ,  $M(\varphi, c)$  is related to the diffusion coefficients  $D_L$  and  $D_S$  (liquid and solid, respectively) and the development of equation (4) leads to:

$$\frac{\partial c}{\partial t} = \nabla \cdot \left\{ \left( D_L \frac{1-\varphi}{2} + D_S \frac{1+\varphi}{2} \right) \frac{c}{c_0(\varphi)} \left[ \frac{\nabla c}{c} + \frac{(1-k)c_{L0} \nabla \varphi}{2c_0(\varphi)} \right] \right\} \quad (10)$$

It is common to artificially scale up the value of  $W$ , which is a layer of some atoms of the order of  $10^{-10}$  m [18]. In this way, non-equilibrium effects are magnified at the interface and, to diminish them, the interpolation functions of the model are chosen according to asymptotic analysis. A correction called “anti-trapping current” is also usually applied [16], but it has been neglected in this study. Some other relations derived from asymptotic analysis are the following ones [15,16]:

$$\tau = \lambda W \left( \frac{\beta}{a_1} + a_2 \frac{W}{D_L} \right) \quad (11)$$

$$\frac{W}{d_0} = \frac{\lambda}{a_1} \quad (12)$$

where  $\beta$  is the kinetic coefficient neglected in this study,  $d_0$  is the capillary length defined as  $d_0 = \gamma P / [T_{mA} R (1-k)^2 \rho c_{L0}]$ , and  $a_1 = 5\sqrt{2}/8$  and  $a_2 = 47/75$  according to asymptotic analysis.

## 2.2 Tracking of crystal orientation

Nucleation models assign specific crystal orientations to nuclei (in general, one angle  $\theta$  in 2D simulations where only  $\langle 10\bar{1}0 \rangle$  directions are considered as preferential growth directions) and growth models take them into account, since each dendrite grows according to its crystal orientation. For the sake of simplicity, the liquid phase is assumed to have a uniform reference value or random values of crystal orientation. There are therefore two aspects that the solidification phase-field model must include: the crystal orientation of each point must be tracked according to the dendrite to which it belongs, and the solution of the evolution equations must consider the local crystal orientation to apply anisotropy relations. Thus, equation (5) becomes  $W = W_0 \{1 + \varepsilon_c \cos[6(\alpha - \theta)]\}$ , where  $\theta$  represents a rotation of the c-axis of the HCP lattice in the X-Y plane.

In this sense, an orientational energy term could be added to the free energy functional  $F$  in equation (1), to account for the effect of grain boundaries [27,28]. In this study, this additional term is not considered because dendritic growth is expected to slow down during eutectic solidification, and contacts between dendrites should therefore be rare. Consequently, no orientational energy term is added to solve equations (3) and (4), and the partial derivative of  $W$  with respect to  $\theta$  is neglected. However, the crystal orientation  $\theta$  is tracked according to the orientational energy density form proposed by Henry *et al.* [29] and an evolution equation of the Ginzburg-Landau form:

$$f_{ori} = H_\theta p(\varphi) (\nabla \theta)^2 \quad (13)$$

$$\begin{aligned} \frac{\partial \theta}{\partial t} &= -M_\theta(\varphi) \frac{\delta F(\varphi, \nabla \theta)}{\delta \theta} \\ &= M_\theta(\varphi) \nabla \cdot [2H_\theta p(\varphi) \nabla \theta] \end{aligned} \quad (14)$$

where  $H_\theta$  is a constant of proportionality,  $p(\varphi)$  is an

interpolation function between the liquid and solid phases and  $M_\theta(\varphi)$  is the associated mobility.  $M_\theta(\varphi)$  and  $p(\varphi)$  are chosen so that  $M_\theta(\varphi)$  be zero in the solid phase and  $p(\varphi)$  be zero in the liquid phase, tending to infinity in the other phase:

$$p(\varphi) = \frac{2(\varphi+1)^3}{(\varphi-1)^2} \quad (15)$$

$$M_\theta(\varphi) = M_0 \frac{2(\varphi-1)^2}{(\varphi+1)^2} \quad (16)$$

To solve equation (14), only the orientational energy density term is considered in the free energy functional, and both partial derivatives with respect to  $\varphi$  and  $\nabla\theta$  are calculated. The evolution of crystal orientation is therefore partially coupled to the phase-field equation, i.e.  $\theta$  is tracked to correctly apply surface tension anisotropy during dendritic growth, without affecting the evolution of phase transformation and diffusion.

### 3. Finite Element Simulations and Discussion of Results

#### 3.1 Choice of parameters

The input parameters for the simulations of Zn4.67Al0.43Mg are detailed in Table 1. The rest of the parameters are calculated using the relations given in the previous section, except for the temperature T and

**Table 1. Input parameters of the model**

Parameter	Value	Units	Source
$k$	0.233	-	Estimated from COST507 [33]
$c_{nom}$	11.62	at.%	-
$m$	-364	K	Estimated from COST507 [33]
$D_L$	$2 \cdot 10^{-9}$	$m^2/s$	Estimated from [34]
$D_S$	0.0	$m^2/s$	-
$\varepsilon_c$	0.1	-	-
$\rho$	6350	$kg/m^3$	Estimated from [35]
$T_{liquidus}$	650.5	K	Estimated from COST507 [33]
$P$	63.41	$g/mol$	-
$\gamma$	0.09	$J/m^2$	Estimated from [36,37]
$H_\theta$	$5.17 \cdot 10^6$	$J/m$	-
$M_0$	4.71	$m^3/(J s)$	-

the “interface thickness”  $W$ , which are chosen to set a certain thermal undercooling and to manage numerical aspects, respectively. The thermal undercooling is set to 10 °C for 1D simulations and to 20 °C for 2D simulations. The space and time factors used to adimensionalise the equations are  $W_0$  and  $\tau$ . The simulations are performed in a uniformly meshed domain of quadrangle linear elements, with zero-flux boundary conditions for  $\varphi$ ,  $c$  and  $\theta$ .

#### 3.2 1D simulations

1D simulations are performed to assess the correspondence between the numerical results of the phase-field model and the analytical solutions for steadily growing planar precipitates [38]. The grid size is set to  $\Delta x = 0.5W_0$  and the total length of the simulation domain is  $500W_0$ , where  $W_0$  is defined for each simulation so that  $W_0/d_0 = 10$ . In the initial state, a nucleus of size  $5W_0$  is placed on one side of the system and the evolution of the solid-liquid interface, as well as the concentration profile are tracked along the simulation. Three values of the initial supersaturation  $\Omega_c$  are tested ( $\Omega_{c1} = 0.25$ ,  $\Omega_{c2} = 0.78$  and  $\Omega_{c3} = 0.95$ ) and, according to equation (18), each of these values is associated with an initial nominal concentration of the liquid phase ( $c_{nom1} = 0.116$ ,  $c_{nom2} = 0.058$  and  $c_{nom3} = 0.039$ ).

The growth velocity of the solid phase is evaluated by measuring the displacement in time of the solid-liquid interface at  $\varphi = 0$ , and its analytical expression is as follows [38]:

$$v(t) = \frac{\lambda_c \sqrt{D_L}}{2\sqrt{t}} \quad (17)$$

where  $\lambda_c$  is calculated from  $\Omega_c$ :

$$\Omega_c = \frac{c_{nom} - c_{L0}}{c_{S0} - c_{L0}} = \frac{\sqrt{\pi}}{2} \lambda_c \exp\left(\frac{\lambda_c^2}{4}\right) \operatorname{erfc}\left(\frac{\lambda_c}{2}\right) \quad (18)$$

Fig. 1 shows the numerical and analytical results of the growth velocity for the three supersaturation values. The convergence of the simulation results was checked for different  $\Delta x$  and  $W_0/d_0$  values, as illustrated by the simulation results for  $\Delta x = 0.25W_0$  and  $W_0/d_0 = 5$  in the case of  $\Omega_{c1}$ . The numerical results are fitted with curves of type  $A/\sqrt{t}$  where A is a constant coefficient, and an

increase in velocity is observed when the value of  $\Omega_c$  is increased in both numerical and analytical results. This corroborates that supersaturated systems are further from thermodynamic equilibrium. Nonetheless, the numerical and analytical results do not match quantitatively, leading to errors of  $e_1 = 4.5 \cdot 10^{-4}$  m/s,  $e_2 = 2.9 \cdot 10^{-3}$  m/s and  $e_3 = 10^{-2}$  m/s between the fit curves and the analytical results at the end of the simulations. These differences are reasonable since the analytical solution does not consider temperature effects. In the case of  $\Omega_{c2}$  and  $\Omega_{c3}$ , the marked drops in the growth velocities by the end of the simulations are boundary effects due to the limited simulation domain.

Profiles of solute concentration can also be tracked and analytically calculated. Their evolution in the liquid phase is given by the following expression [20]:

$$c(x,t) = c_{nom} + (c_{L0} - c_{nom}) \frac{\operatorname{erfc}\left\{\frac{\lambda_c[x(t) - x_0(0)]}{2[x_0(t) - x_0(0)]}\right\}}{\operatorname{erfc}\left(\frac{\lambda_c}{2}\right)} \quad (19)$$

where  $x(t)$  is the spatial coordinate,  $x_0(t)$  is the position of the solid-liquid interface at time  $t$ , and  $x_0(0)$  is the position of the solid-liquid interface in the initial state. Fig. 2 compares the results of two simulations with this analytical solution at different moments of the simulations. As the results correspond to the liquid phase, the initial values of these curves are the concentration peaks at the solid-liquid interface. The lower the value of  $\Omega_c$  is, the closer to the interface the concentration in the liquid reaches its bulk value with respect to the analytical solution. In addition, the numerical peak concentrations

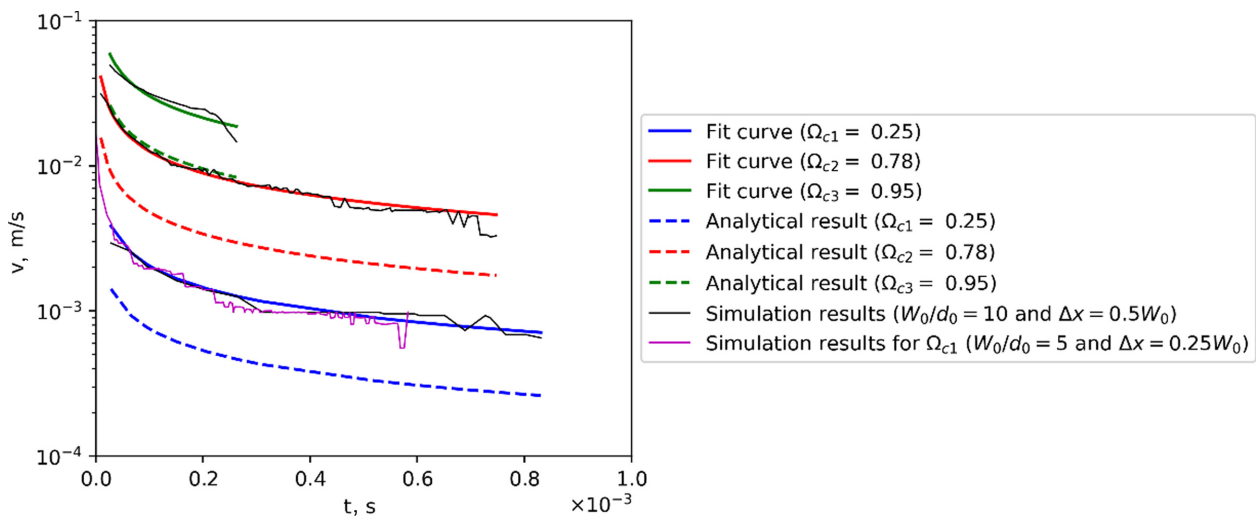


Fig. 1. Profiles of growth velocity for different supersaturation values

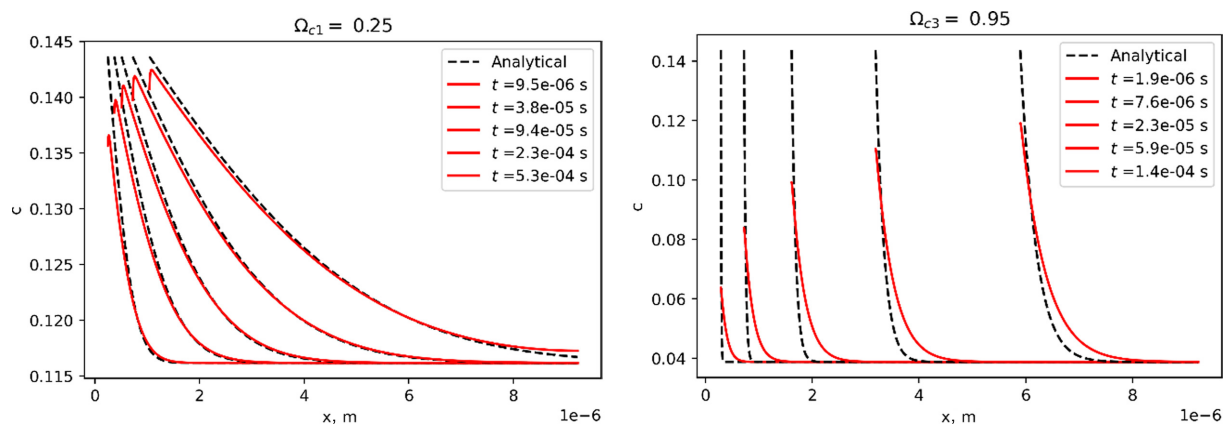


Fig. 2. Profiles of solute concentration in the liquid for different supersaturation values

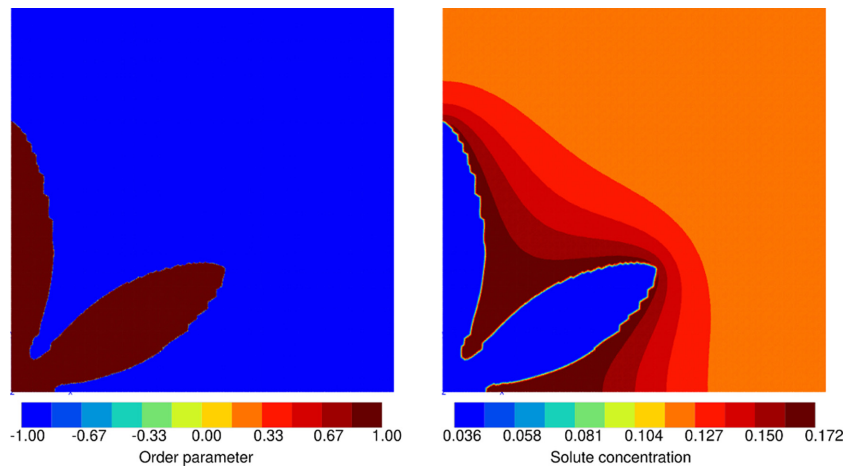
become higher with time, while the analytical peak concentrations remain constant because the concentration at the solid-liquid interface is a fixed boundary condition in [38]. The curves affected by boundary effects are not shown in this case, because the analytical expression is no longer valid.

**3.3 Isothermal dendritic solidification**

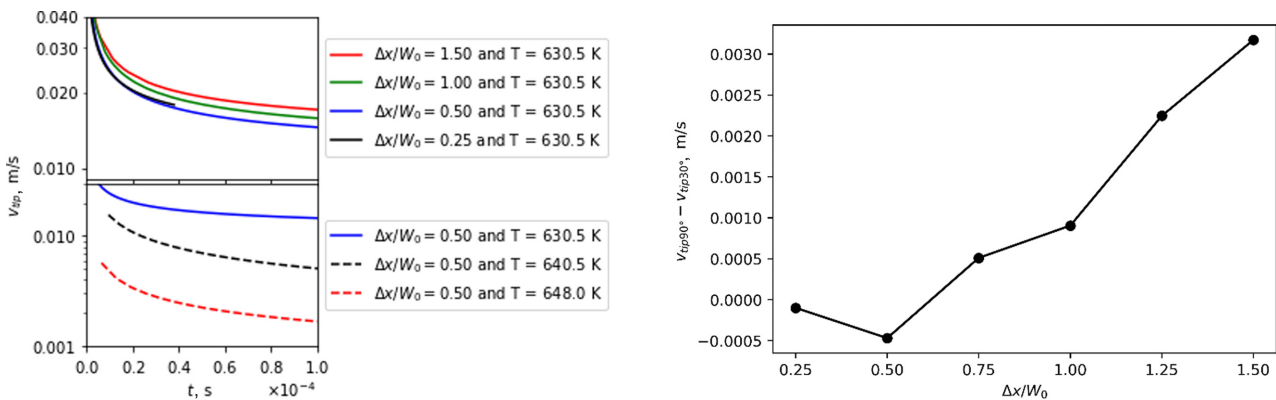
Quarters of dendrites are simulated in a 2D mesh, conveniently oriented to take advantage of the 6-fold symmetry (the first branch grows at 30° from the X-axis and the second at 90°). The “interface thickness”  $W_0$  is fixed at 15.5 nm so that  $W_0/d_0 = 10$ , and the inserted nuclei have a radius of  $4W_0$ . The convergence of the results is examined by varying the grid size  $\Delta x$  between  $0.25 W_0$  and  $1.5 W_0$ . Fig. 3 shows the fields  $\varphi$  and  $c$  of the simulation corresponding to  $\Delta x = W_0$ , where

segregation of solute in the liquid near to the solid-liquid interface is visible. This simulation of 502,002 degrees of freedom was run in 20 cores and took 3.4 days of wall-clock time. The simulation domain is limited to a total size of  $7.75 \times 7.75 \mu\text{m}^2$  due to the high computational cost. Hence, the results of this study represent only the first growth stage of zinc dendrites, which actually have a total size of a few tens of microns.

The growth velocities of the primary branches in directions  $\langle 10\bar{1}0 \rangle$  can be evaluated by measuring the displacement in time of the points where  $\varphi = 0$ . When comparing these dendrite tip velocities for different  $\Delta x$  in Fig. 4, it is observed that the values of different branches converge when  $\Delta x$  is below  $0.5W_0$ . Thus, growth velocity becomes independent of grid anisotropy and discretization around this element size. Due to the sudden thermal undercooling of 20 °C, the velocities



**Fig. 3.** Phase field  $\varphi$  (left) and concentration field  $c$  (right) of isothermal simulation ( $t = 499\tau = 0.33$  ms)



**Fig. 4.** Fitted tip velocity curves of type  $A/\sqrt{t} + B$  for dendrite branch at 90° (left), and differences in fitted tip velocities between the branches at 30° and 90° at the end of the simulations for different  $\Delta x$  (right)



obtained are 1-2 orders of magnitude higher than those calculated for a galvanising test machine [39]. The dashed curves in Fig. 4 correspond to simulations for lower undercoolings ( $T = 640.5$  K and  $T = 648$  K), where a drastic reduction in dendrite tip velocity is observed. The results should therefore be close to reasonable values in the case of realistic thermal paths.

In order to assess the concentration profiles, the solute concentrations along the dendrite branches are compared with the values obtained by the Gibbs-Thomson relation without the kinetic term. In fact, as no diffusion is considered in the solid phase, the concentration on the solid side of the interface obtained from equation (20) corresponds to the final concentration in the solid:

$$\frac{c_S}{c_{L0}} = k \left( 1 - \frac{(1-k)d_0}{\rho_{tip}} \right) \quad (20)$$

where the dendrite tip radius  $\rho_{tip}$  is calculated from simulation results according to Vakili *et al.* [40] (a

negative sign is added to obtain positive tip radii in the solid-to-liquid direction):

$$\frac{1}{\rho_{tip}} = -\frac{1}{\|\nabla\phi\|} \left( \nabla^2\phi - \frac{\nabla\phi \cdot \nabla\|\nabla\phi\|}{\|\nabla\phi\|} \right) \quad (21)$$

This implies that the  $c_s$  value obtained from equation (20) is not completely analytical, but it serves as a reference for comparison. For example, Fig. 5 shows the concentration profile along a dendrite branch for  $\Delta x = W_0$ , where the mean absolute error of the simulation result with respect to the semi-analytical result from the Gibbs-Thomson relation is 0.028 at.%. The detail in Fig. 5 shows that the semi-analytically obtained concentration is lower than the concentration profile for a flat solid-liquid interface where  $\rho_{tip}$  tends to infinity ( $c_{s0} = k c_{L0}$ ), which is the effect of introducing a positive curvature in the Gibbs-Thomson relation. The semi-analytical concentration is also lower than the simulation result, and this difference is most likely due to solute trapping

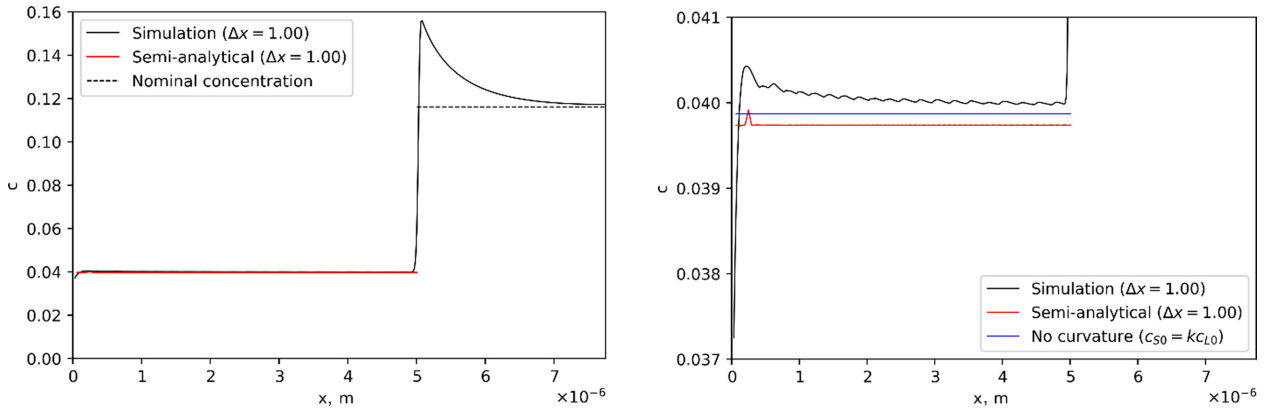


Fig. 5. Solute concentration profile along a dendrite branch (left) and its detail of the solid portion (right)

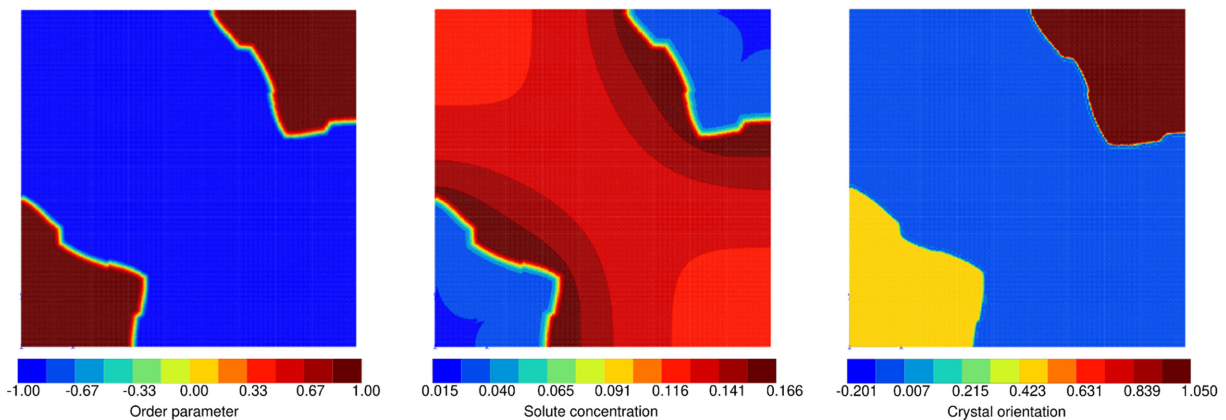


Fig. 6. The three field variables  $\phi$ ,  $c$  and  $\theta$  in a multi-dendrite simulation ( $t = 33\tau = 22 \mu s$ )

and the error associated with the numerical evaluation of  $\rho_{tip}$ . Concentration peaks on the liquid side of the solid-liquid interface are due to solute segregation in the vicinity of dendrites (see concentration field in Fig. 3), i.e. there is little diffusion in the liquid compared to the rejection of atoms by the solid.

### 3.4 Tracking of crystal orientation in multi-dendrite simulations

Crystal orientation is implemented as explained in section 2.2. Fig. 6 shows the three field variables for the growth of two initial nuclei of size  $4W_0$ . The crystal orientation in the liquid is set to  $0^\circ$ , whereas the solid grains have crystal orientations of  $30^\circ$  and  $60^\circ$ . In this case, the simulation domain has a total size of  $1.6 \times 1.6 \mu\text{m}^2$ , and  $W_0$  is fixed at 15.5 nm so that  $W_0/d_0 = 10$ .

## 4. Conclusions and Outlook

In this work, a phase-field model for dendritic solidification is applied to the ZnAlMg system, by treating it as a pseudo-binary dilute alloy. In addition to the phase transformation, the model gives the evolution of the solute concentration field and tracks the crystal orientation of the solidified grains. The latter is implemented with partial coupling, so that only surface tension anisotropy aspects of the solidification process be affected. 1D and 2D finite element simulations are performed with constant thermal undercooling and nuclei are introduced as initial conditions. The results are qualitatively consistent with analytical calculations of concentration profiles and growth velocity. To achieve convergence and quantitative validation of the results, a grid size of half the characteristic interface thickness is required, which limits the spatial domain of the simulations.

As the study aims at multi-dendrite solidification simulations of realistic dimensions for ZnAlMg coatings, subsequent work will include further parametric studies and the implementation of computational cost reduction techniques. A gain in accuracy should also be expected, if terms such as the “anti-trapping current”, the kinetic effects and the diffusion in the solid phase were considered. Furthermore, other thermal paths can be simulated to approximate real solidification conditions,

as well as quasi-3D models to account for a greater variety of crystal orientations. These aspects and comparisons with experimental data will also be included and discussed in future work.

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