Phase-field modeling of the columnar-to-equiaxed transition in neopentylglycol-camphor alloy solidification

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Abstract. We have performed phase field simulations in order to explore the effect of equiaxed grain nucleation undercooling on the columnar to equiaxed transition "CET" in the NPG-DC alloy system. Our phase field model is based on the multiphase-field method. The simulation parameters are adapted to a microgravity experiment performed under purely diffusive growth conditions. The experimental investigation is made during the sounding rocket campaign TEXUS-47.

1. Introduction
Multiscale and multiphase modeling of solidification is a subject of active research in materials science. Understanding the effects of macroscopic process conditions on the microstructure evolution is important to assure e.g. the mechanical properties of the casting. The columnar to equiaxed transition (CET) in dendritic solidification describes a discontinuous change in microstructure and is a common morphological transition in technical castings. The microstructure is called columnar if the dendritic growth tends to one direction, whereas equiaxed grains are oriented in all directions. The CET depends on the thermal conditions defined on the macroscopic scale, the local undercooling near the solid-liquid interface, which is determined by the dendritic morphology on the microscale, the thermophysical properties of the alloy and the nucleation mechanism of equiaxed dendrites. The Neopentylglycol-DCamphor (NPG-DC) alloy is a transparent organic alloy which allows an in-situ observation of the solidification microstructure at temperatures closed to ambient. This alloy is used as analogue system with metallic alloys, which are opaque, and only enable a post-mortem analysis of the structure. We have performed simulations on the CET in the NPG-DC alloy system using a multi-phase field model [1, 2, 3] in 2D and 3D, in the limit of diffusive mass transport. Additional effects of thermosolutal convection and buoyancy or sedimentation can be neglected under low-gravity conditions.
2. Phase Field Model

In the present work, the multi-phase field formulation proposed by Steinbach et al [1] and further developed towards the coupling to thermodynamic databases [3] is employed to describe the morphological evolution during the solid-liquid phase transformation. The phase field method relies on a phase field parameter ($\phi$) which varies continuously from liquid "l" ($\phi=0$) to solid "s" ($\phi=1$) along the solid-liquid interface of width $\eta$. The evolution of the phase field parameter in time is given by:

$$\dot{\phi}_s = M_{sl}^a(\vec{n}) [\sigma_{sl}^a(\vec{n}) K_{sl} + w \Delta G_{sl}]$$ (1)

with:

$$K_{sl} = \phi_s \nabla^2 \phi_l - \phi_l \nabla^2 \phi_s + \frac{\pi^2}{\eta^2} (\phi_s - \phi_l)$$ (2)

$$w = \frac{\pi}{\eta} \sqrt{\phi_s \phi_l}$$ (3)

$$\Delta G_{sl} = -f_s(c_s) + f_l(c_l) + \vec{\mu}(c_s - c_l)$$ (4)

where $M_{sl}^a(\vec{n})$ is the anisotropic interfacial mobility between liquid and solid as a function of the interface orientation (described by the normal $\vec{n}$) and $\sigma_{sl}^a(\vec{n})$ is the effective anisotropic surface energy. The anisotropic functions for the both parameters are written in expansion in terms of normalized spherical harmonics $y_l$ selected under consideration of the specific crystal lattice periodicity [4]:

$$M_{sl}^a(\vec{n}) = M_{sl} \left( 1 + \sum_l \epsilon_{sl}^{M} y_l(\vec{n}) \right) \quad \text{and} \quad \sigma_{sl}^a(\vec{n}) = \sigma_{sl} \left( \sum_l \epsilon_{sl}^{\sigma} y_l(\vec{n}) \right)$$

where $M_{sl}$ and $\sigma_{sl}$ are the isotropic phase field mobility and surface energy, respectively. The thermodynamic driving force $\Delta G_{sl}$ depends on the respective bulk free energies $f_s(c_s)$ and $f_l(c_l)$, determined using a thermodynamic database, $\vec{\mu}$ is the generalized chemical potential introduced to conserve local concentration due to the constraint of quasi-equilibrium. This constraint postulates that all the reduced chemical potentials are the same for the coexisting phases i.e.

$$\vec{\mu} = \vec{\mu}_s(c_s(\vec{x})) = \vec{\mu}_l(c_l(\vec{x}))$$

The evolution of the concentration field is given by:

$$\dot{c} = \nabla (\phi_s D_s \nabla c_s) + \nabla (\phi_l D_l \nabla c_l),$$ (5)

where $D_s$ and $D_l$ are the diffusion coefficients in the solid and liquid phase, respectively. We have converted the liquid concentration ($c_l$) into a constitutional undercooling in the melt ($\Delta T_c$) using the relation $\Delta T_c = T_l(c_l) - T$ where $T_l(c_l)$ is the liquidus temperature and $T$ is the local temperature defined by:

$$T = T_B - c_r \cdot t + G \cdot z$$ (6)

where $T_B$ is the temperature at the bottom of the domain, $c_r$ is the cooling rate, $G$ is the thermal gradient.
3. Microgravity experiment
The experiment TRACE was performed in a transparent sheet-like cell with 1 mm thickness. Details of the experimental set-up and procedure are given in [5, 6]. Solidification was controlled by applying temperatures and cooling rates at the bottom and the top of the solidification volume. While the thermal gradient was almost constant, the cooling-rate was increased by a factor of 10 from -0.2 K/min for columnar growth to -2.0 K/min for the transition to equiaxed dendritic growth. Table 1 summarizes the experimental, thermodynamical and thermophysical parameters, accompanied by some numerical parameters needed for the phase-field simulations. Figure 1 shows an image taken from the experiment at steady-state columnar growth, and figure 2 during the CET, which occurs 375 s after increasing the cooling-rate to -2.0 K/min. Between the two images, the columnar front was grown 1.5-2.0 mm.

Figure 1. Microstructure observed during steady state columnar growth in the TRACE experiment. The width of the cell is 20 mm

Figure 2. Microstructure observed during CET in the TRACE experiment.

4. Numerical simulation
The physical and numerical parameters that we used in our simulations are listed in table 1. The MICRESS code was used to solve numerically the phase field (Eqn 1 to 4) and diffusion equation (Eqn 5). Two-dimensional and three dimensional phase field simulations were performed. Concerning the two-dimensional calculation domain, a rectangular box of 450 µm height was used. The calculations start with a homogeneous melt at a given temperature gradient (see table 1) where three nuclei of solid primary phase are disposed at some undercooling and equal spacings on the bottom side of the calculation domain. We performed a study of the influence of dendrite spacing by varying the width of the calculation domain between 450 µm and 1350 µm. The grid spacing for all simulations is 0.75 µm. For the three-dimensional calculations, the simulation domain is a box of 150 × 150 × 450 µm³. Only one nuclei is disposed in the corner of the calculation domain. In all simulations, the temperature gradient is fixed and constant in one direction. Only the cooling rate is changing from -0.2 K/min to -2.0 K/min to promote CET. A moving calculation domain was used in which the distance from the dendrite tips to the top boundary of the moving calculation domain is fixed. In a first stage of the simulation, a columnar dendritic structure is allowed to evolve in order to reach a steady state growth. The cooling rate is fixed to -0.2 K/min. In a second stage, the cooling rate is increased to -2.0 K/min and nucleation is allowed, using a critical nucleation undercooling and nucleation
density for randomly oriented seeds in the melt. We suppose that the formation of equiaxed dendrites is controlled by heterogeneous nucleation during the microgravity experiment. The critical nucleation of undercooling is varied during the different simulations. The nucleation density is supposed to be equal to the equiaxed grain density ($N_e$, Tab. 1).

Table 1. Physical and numerical parameters used in our simulations

| Parameter                                      | Value                              |
|------------------------------------------------|------------------------------------|
| Concentration ($c_{DC}^0$)                     | 37.5 wt.%                          |
| Equiaxed grain density [5] ($N_e$)              | $5 \cdot 10^8$ m$^{-3}$            |
| Temperature gradient [5] ($G$)                  | 1650 K/m                           |
| Interface thickness ($\eta$)                    | 3 $\mu$m                           |
| Diffusion coefficient in liquid [5] ($D_l$)     | $6.1 \cdot 10^{-11}$ m$^2$/s       |
| Diffusion coefficient in solid ($D_s$)          | 0 m$^2$/s                          |
| Surface energy ($\sigma_{sl}$)                  | $6 \cdot 10^{-3}$ J/m$^2$          |
| Phase field mobility ($M_{sl}$)                 | $1 \cdot 10^{-12}$ m$^4$/Js        |
| Liquidus slope [5] ($m_l$)                      | $-1.65$ K/wt%                      |
| Partition coefficient ($k$)                     | $7.75 \cdot 10^{-2}$               |
| Static anisotropy ($\epsilon_{sl}^s$)          | 1.6 %                              |
| Kinetic anisotropy ($\epsilon_{sl}^M$)         | 15%                                |

5. Results and discussion

5.1. Steady state

Steady state columnar growth in 2D is obtained after 15000 s. In figure 3, we have represented the $\Delta T_c$-field at $t=15000$ s (section 2). We can distinguish three columnar dendrites with secondary branches corresponding to the three initials nuclei growing along the temperature gradient. In figure 4 undercooling profiles are shown along the dendrite tip (solid line 1) and in between the dendrites (dashed line 2). In the insert of figure 4, the solid and dashed horizontal lines correspond to the maximal undercoolings for the profiles along the dendrite tip and between the dendrites respectively. In steady state growth, the maximum of $\Delta T_c$ is constant and equal to approximately 18.1 K. As observed by Badillo and Beckermann [9] and Dong and Lee [10], the maximum undercooling is situated on the symmetry line between columnar branches. Several 2D simulations were performed using different experimentally observed dendrites spacings of 150, 300, 450 $\mu$m corresponding to 450, 900, 1350 $\mu$m calculation domain width. We have observed differences smaller than 1% concerning the value of the final maximum constitutional undercooling in the bulk. In all cases the results shows that the maximum constitutional undercooling is located between the dendrites.

To be able to describe the growth of several dendrites in 3D with a spacing of 300 $\mu$m we used symmetry conditions on the calculations domain sides to simulate the presence of the other dendrites. On figure 5, we have plotted the phase field contour ($\phi=0.5$) of a dendrite at $t=8000$ s, for a crystallographic orientation of 45°. For the orientation of 0°, the secondary arms are growing along the domain sides. Like the 2D simulations, we observed a maximal solutal undercooling between the dendrites equal to 7.8 K. Orientation (0° or 45°) plays also a minor role on the value of undercooling. We have noticed that the time to reach constant value of the constitutional undercooling was lower in 3D (around 8000 s) than in 2D (15000 s).

We performed a comparison with the predictions of the KGT-model [7, 8] concerning the value of the constitutional undercooling in 2D and 3D. In the KGT-model, the undercooling is calculated at the dendrite tip, but the differences to the maximum bulk value are small here.
Furthermore a stability constant $\sigma^*$ appears, which is $0.0253$ ($= 1/(4\pi^2)$) in the standard model. It was found [6] that a value of 0.007 should be used to obtain best fit to experiments. Using these two different values of $\sigma^*$, we have summarized the values for the undercooling obtained from the KGT model in 2D ($\Delta T_{c2D}$), in 3D ($\Delta T_{c3D}$) and phase field in table 2. We have seen that the phase field simulations result in values of constitutional undercooling of 7.8 K in 3D and 18.1 K in 2D giving a ratio ($Q$) of 2.30. The geometry that we obtained by phase field can not be described correctly by the KGT model, which assumes a parabolic shape. Nevertheless, we can remark that the 2D result of phase field is an average of the KGT values. For 3D simulation, the phase field results are above the highest KGT prediction, but close to the value ($\sigma^*=0.007$) used to fit the experimental results [6].
Table 2. Constitutional undercooling using the KGT model [7, 8] and phase field results

|               | $\Delta T_{c}^{2D}$ (K) | $\Delta T_{c}^{3D}$ (K) | $Q=\Delta T_{c}^{2D}/\Delta T_{c}^{3D}$ |
|---------------|------------------------|------------------------|------------------------------------------|
| KGT $\sigma^*=0.0253$ | 15.5                  | 4.5                    | 3.4                                      |
| KGT $\sigma^*=0.007$   | 21.3                  | 7.1                    | 3.0                                      |
| Phase field         | 18.1                  | 7.8                    | 2.3                                      |

5.2. CET

We introduced seeds randomly positioned and oriented in liquid zone of the simulation domain. The initial microstructure was taken from the previous steady state simulation. We have used the same nucleation density $N_e$ (Tab. 1) for all simulations, only the nucleation undercooling ($\Delta T_n$) varies between 8.5 K and 20 K for 3D and 17 K and 27 K for 2D simulations. For 2D simulations, if the nucleation undercooling is lower than 27 K, we observed equiaxed grains at the front of columnar dendrites (figure 6). Above 27 K, nucleation is not possible and the microstructure remains columnar (figure 7). For 3D simulations below 20 K, CET occurs (figure 8). Above 20 K, the dendritic structure remains columnar (figure 9). It is also important to notice that 3D simulation allow to observe the change of microstructure of the columnar zone. We can clearly distinguish that ternary arms are developing orthogonal to secondary arms side because of the change of the cooling rate. The experimental measurements [6] show that CET occurs with the nucleation undercooling of nuclei situated between 8.5 K and 12 K.

Before CET occurs and the new nucleated grains blocked the columnar dendrites, a transient state is experimentally observed where the columnar dendrites continue to grow on a distance between 1.5 and 2.0 mm. On figure 10, we have plotted the length of this transition zone versus the different nucleation undercooling that we used for the 3D and 2D simulation. The experimental measurement are represented by the gray square. We see that for low value of nucleation undercooling the 3D-model is close to the experimental results. Nevertheless the fact that the 3D phase field results are not localised into the grey domain can be attributed to heat redistribution during the cooling rate change. In experiments, the redistribution of heat

Figure 6. Concentration map (camphor %wt) during CET ($\Delta T_n=25$ K). Width of the domain : 1350 µm

Figure 7. Concentration map (camphor %wt) when no CET occurs ($\Delta T_n=27$ K). Width of the domain : 1350 µm
is continuously, not immediately as in our simulation. During this change of cooling rate the dendrite grows further during experiments than in simulations. For the 2D results, we see that the value of the nucleation undercooling are far from experiments.
6. Conclusion
We have shown in this work that phase field model can be very efficient in modeling the columnar to equiaxed transition. The first 3D phase field simulations of CET have been presented. The model describe correctly the CET using the experimental value of nucleation undercoolings and predicts with good accuracy the length of the columnar zone before CET. But the most important is that 2D simulations are not describing experiments as good as 3D simulations. The value of nucleation undercoolings, and the transition length for example, are very far from experiments.

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Figure 10. Length of the transition zone versus nucleation undercooling