Discussions on the non-equilibrium effects in the quantitative phase field model of binary alloys*

Wang Zhi-Jun(王志军), Wang Jin-Cheng(王锦程)†, and Yang Gen-Cang(杨根仓)

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, *China*

(Received 23 October 2009; revised manuscript received 20 January 2010)

All the quantitative phase field models try to get rid of the artificial factors of solutal drag, interface diffusion and interface stretch in the diffuse interface. These artificial non-equilibrium effects due to the introducing of diffuse interface are analysed based on the thermodynamic status across the diffuse interface in the quantitative phase field model of binary alloys. Results indicate that the non-equilibrium effects are related to the negative driving force in the local region of solid side across the diffuse interface. The negative driving force results from the fact that the phase field model is derived from equilibrium condition but used to simulate the non-equilibrium solidification process. The interface thickness dependence of the non-equilibrium effects and its restriction on the large scale simulation are also discussed.

Keywords: phase field model, solidification, diffuse interface
PACC: 8130F, 6810C, 0570F

1. Introduction

The phase field method has been a powerful tool in microstructural evolution simulation with the development of computer and numerical methods. It has been widely used in the research of solidification theory.[1−8] In phase field method, the free-boundary problem is treated by solving the multi-field coupled governing equations to avoid tracking the complex interface and therefore the topology changes can be easily treated. However, phase field method is strongly restricted by the huge discrepancy between the simulation scale and the thickness of the diffusion interface. Realistic simulation of solidification microstructures needs an exorbitantly fine grid to resolve the steep gradients inside the diffuse interface, which makes computations intractable. By properly increasing the interface thickness, the simulation efficient can be significant improved. However, the increase of interface thickness brings artificial non-equilibrium effects to the simulation results. The convergence of simulation results requires small interface thickness. Recently the presence of the quantitative phase field models presented by Karma[6−8] has improved considerably the computation efficiency by a 'thin-interface' asymptotic analysis which puts the phase field method forward to the more realistic application. In the quantitative phase field models, the artificial non-equilibrium effects were compensated by properly selecting the interpolated functions and adding anti-trapping current (ATC) term for binary alloys. Accordingly, the artificial non-equilibrium effects from the diffuse interface are the most concerned issues in quantitative phase field models.

The non-equilibrium effects in the phase field model characterised in the 'thin-interface' asymptotic analysis, including surface diffusion, interface stretching and discontinuity chemistry potential across the interface, are the most considered problems in quantitative phase field models of binary alloys.[9] In the first phase field model of binary alloys (WBM model) proposed by Wheeler *et al.*,[10] the finite interface thickness introduces an extra chemical potential which leads to discontinuity of the chemical potential across the diffuse interface. Later, Kim–Kim-Suzuki[11] (KKS) removed the extra chemical potential by the proper treatment of equal chemical potential across the diffuse interface. In KKS model, the composition in the diffuse interface is a numerical solution, which cannot be analytical solved. In the quantitative phase field model with ATC, the restriction of interface thickness from the extra chemical potential has been removed analytically.[8,12,13] However, in phase field simulation the interface thickness dependent non-equilibrium effects cannot be avoided totally. As the interface thickness increases, simula-

*Project supported by the fund of the State Key Laboratory of Solidification Processing in NWPU, China (Grants Nos. 17-TZ-2007, 03-TP-2008, and 24-TZ-2009) and the Doctorate Foundation of Northwestern Polytechnical University.
†Corresponding author. E-mail: jchwang@nwpu.edu.cn
© 2010 Chinese Physical Society and IOP Publishing Ltd

tion results such as the tip velocity, tip radius and solutal distribution will be beyond convergence. The evaluation of the non-equilibrium effects in the simulation process is still an open question. The origin of the interface thickness dependent non-equilibrium effects and its intrinsic relationship with the interface thickness need to be further discussed, which may potentially improve the efficiency of phase field method. Herein, the non-equilibrium effects are revealed from the bulk free energy density across the solid/liquid diffuse interface according to thermodynamic analysis in the quantitative phase field model of binary alloys. The local non-equilibrium state across the diffuse interface is numerically examined by phase field simulation results.

2. The quantitative phase field model of binary alloys

The quantitative phase field model with ATC term directly follows the formulations given by Ramirez *et al.*[8] (full derivations can be found in the article). The model is based on the phenomenological free energy functional F defined over the system volume V,

$$F = \int \mathrm{d}V \left[\frac{\varepsilon_\phi^2}{2} |\nabla\phi|^2 + f_{\mathrm{AB}}(\phi, c, T) \right], \tag{1}$$

where ε_ϕ is the associated gradient energy coefficient, ϕ is the phase field variable, c is the mole fraction of solute B, and T is the temperature. The first term in the bracket is the gradient energy related to the surface tension energy, and $f_{\mathrm{AB}}(\phi, c, T)$ is the bulk free energy density of a binary mixture of A and B atoms (molecules),

$$f_{\mathrm{AB}}(\phi, c, T) = f(\phi, T_{\mathrm{m}}) + f_{\mathrm{mix}}(\phi, c, T), \tag{2}$$

where

$$f(\phi, T_{\mathrm{m}}) = H\left(-\phi^2/2/ + \phi^4/4\right) \tag{3}$$

is the standard double-well function with the barrier height coefficient H, and

$$f_{\mathrm{mix}}(\phi, c, T) = f^{\mathrm{A}}(T_{\mathrm{m}}) - (T - T_{\mathrm{m}})s(\phi) + \frac{RT_{\mathrm{m}}}{v_0}(c\ln c - c) + \varepsilon(\phi)c \tag{4}$$

is the hybrid free energies of liquid phase and solid phase for a dilute binary alloys. Here, $f^{\mathrm{A}}(T_{\mathrm{m}})$ is the free energy for pure A at melting point T_{m}, R is the gas constant and v_0 is the molar volume of A, and

$$s(\phi) = \frac{s_{\mathrm{s}} + s_{\mathrm{l}}}{2} - \tilde{g}(\phi)\frac{L}{2T_{\mathrm{m}}}, \tag{5}$$

$$\varepsilon(\phi) = \frac{\varepsilon_{\mathrm{s}} + \varepsilon_{\mathrm{l}}}{2} + \bar{g}(\phi)\frac{\varepsilon_{\mathrm{s}} - \varepsilon_{\mathrm{l}}}{2}, \tag{6}$$

where s is the parameter related to entropy density, and ε is the parameter related to internal energy density. The subscript s and l indicate the solid phase and liquid phase respectively, $\tilde{g}(\phi)$ and $\bar{g}(\phi)$ are interpolation functions and L is the latent heat per unit volume. According to the equilibrium state condition,

$$\frac{\delta F}{\delta \phi} = 0, \tag{7}$$

$$\frac{\delta F}{\delta c} = \mu_{\mathrm{E}}(T), \tag{8}$$

and the independence of surface tension energy $[\partial_\phi f_{\mathrm{mix}}(\phi, c, T) = 0]$, the relationship between the two different interpolation functions is,

$$\bar{g}(\phi) = \frac{2}{\ln k}\ln\left[\frac{1 + k - (1-k)\tilde{g}(\phi)}{2}\right] - 1, \tag{9}$$

where $\mu_{\mathrm{E}}(T)$ is the chemical potential, k is the equilibrium segregation coefficient.

With the variational formulation $\partial_t\phi = -K_\phi \delta F/\delta\phi$, the phase field equation is

$$\tau\frac{\partial\phi}{\partial t} = W^2\nabla^2\phi + \phi - \phi^3 + \frac{\lambda}{L/c_p}(1-\phi^2)^2 \times\left(\frac{2mc}{1 + k - (1-k)\phi} - (T - T_{\mathrm{m}})\right), \tag{10}$$

where $\tau = 1/(K_\phi H)$, $\lambda = 15L^2/(16Hc_{\mathrm{p}}T_{\mathrm{m}})$, $W = (\varepsilon_\phi/H)^{1/2}$ is the width of the hyperbolic tangent profile of ϕ across the diffuse interface, K_ϕ is a constant, m the liquidus slope and c_{p} the thermal capacity. According to the thin interface analysis, the relations between these parameters are

$$d_0 = a_1 W/\lambda, \quad \tau_0 = a_2\lambda W^2/D, \quad a_1 = 0.8839, \quad a_2 = 0.6267, \tag{11}$$

where d_0 is the thermal capillary length and D the solutal diffusivity in the liquid. The equilibrium solution or the first order solution in the thin interface analysis is $\phi_0(x) = -\tanh(x/(\sqrt{2}W))$. Then the excess free energy of the interface is given by

$$\gamma = \varepsilon_\phi^2\int_{-\infty}^{+\infty}\left(\frac{\mathrm{d}\phi_0}{\mathrm{d}x}\right)^2\mathrm{d}x = \frac{2\sqrt{2}}{3}WH. \tag{12}$$

The solutal diffusion equation is derived through a volume-averaging technique including an additional anti-trapping term that counterbalances the solute trapping effect.[14] Using W and W^2/D as the scale of length and time respectively, the complete two coupled non-dimensional equations can be expressed as

$$\frac{\partial \phi}{\partial t} = \frac{1}{a_2 \lambda}(\nabla^2 \phi + \phi - \phi^3) + \frac{1}{a_2 L/c_\mathrm{p}}(1-\phi^2)^2 \left(\frac{2mc}{1+k-(1-k)\phi} - (T - T_\mathrm{m}) \right), \tag{13}$$

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[\frac{1-\phi}{1+k-(1-k)\phi} \nabla c + \left(\frac{1-\phi}{1+k-(1-k)\phi} + \frac{W}{\sqrt{2}} \frac{\partial \phi}{\partial t} \frac{1}{|\nabla \phi|} \right) \frac{c(1-k)}{1+k-(1-k)\phi} \nabla \phi \right]. \tag{14}$$

3. The non-equilibrium effects relevant to negative driving force

In the phase field model, the phase transformation driving force contributed by the non-equilibrium of liquid and solid phases in thermodynamics is related to the second term on the right-hand side (RHS) of Eq. (13),

$$\partial_\phi f_\mathrm{mix} \propto mc_\mathrm{l} - (T - T_\mathrm{m}), \tag{15}$$

where

$$c_\mathrm{l} = \frac{2mc}{1+k-(1-k)\phi}.$$

Under the equilibrium condition,

$$\partial_\phi f_\mathrm{mix} = mc_\mathrm{l}^0 - (T - T_\mathrm{m}) = 0, \tag{16}$$

where c_l^0 is the equilibrium liquid concentration. During non-equilibrium solidification process, the liquid concentration c_l is smaller than the equilibrium concentration c_l^0 in order to produce the positive driving force $\partial_\phi f_\mathrm{mix} > 0$ as shown in Fig.1.[15]

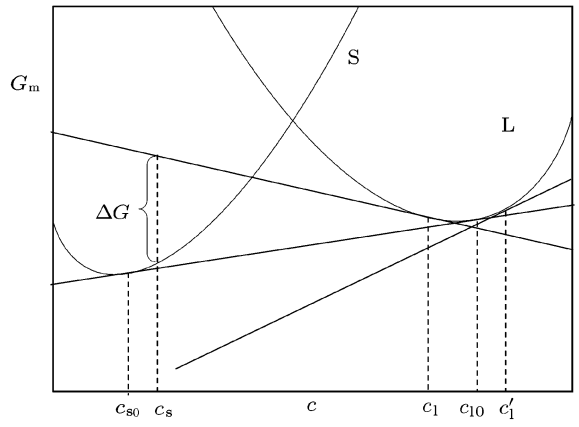


Fig. 1. Sketch of the composition at the interface during solidification process.

According to the Gibbs free energy curves, when $c_\mathrm{l} > c_\mathrm{l}^0$, the relevant solid composition does not exist because the phase transformation driving force ΔG is negative, e.g. the c_l' in Fig. 1. In quantitative phase field model, the condition of $c_\mathrm{l} \leq c_\mathrm{l}^0$ may not be satisfied at some local area across the diffuse interface. In the derivation of quantitative phase field model

$$c(\phi) = \frac{c_\mathrm{l} + c_\mathrm{s}}{2} + \phi \frac{c_\mathrm{l} - c_\mathrm{s}}{2}, \quad k = c_\mathrm{s}/c_\mathrm{l}. \tag{17}$$

The non-equilibrium concentration of solid phase c_s is always a little higher than the equilibrium one c_s^0 during the solidification process. The phase transformation driving force satisfies

$$\begin{aligned} mc_\mathrm{l} - (T - T_\mathrm{M}) &= \frac{mc_\mathrm{s}}{k} - (T - T_\mathrm{M}) \\ &< \frac{mc_{s0}}{k} - (T - T_\mathrm{M}) = 0 \end{aligned} \tag{18}$$

on the solid side of the diffuse interface. Therefore the non-equilibrium distribution of phase field and concentration across the diffuse interface bring about the negative phase transformation driving force at the certain local area where

$$\frac{2mc}{1+k-(1-k)\phi} - (T - T_\mathrm{m}) < 0, \tag{19}$$

which means that the liquid phase is the stable state from the viewpoint of thermodynamics. However, the contribution of the surface tension energy term in the phase field model still drive the mixture of solid and liquid to metastable solid state ($\partial\phi/\partial t > 0$) instead of stable liquid state ($\partial\phi/\partial t < 0$). During the derivation of the phase field model, the surface tension energy is a constant physical parameter in Eq. (12). With the increase of the interface thickness, the energy barrier height coefficient H decreases to keep WH constant. Then the amendment of surface tension becomes lower and the non-equilibrium effects related to the negative driving force will be more obvious. When the surface tension cannot make up for the negative driving force, $\partial\phi/\partial t < 0$ may appear at the certain local area across the diffuse interface. The requirement of $\partial\phi/\partial t > 0$ during the simulation of continuous solidification process can introduce the restriction on the phase field model,

$$\begin{aligned} &\nabla^2 \phi + \phi - \phi^3 + \frac{\lambda}{L/c_\mathrm{p}}(1-\phi^2)^2 \\ &\times \left(\frac{2mc}{1+k-(1-k)\phi} - (T - T_\mathrm{m}) \right) > 0. \end{aligned} \tag{20}$$

According to the relationship of $d_0 = a_1 W/\lambda$ in the phase field model, the limitation on the interface thickness will be

$$\frac{W}{d_0} < \min\left\{ -\frac{\left(\nabla^2\phi + \phi - \phi^3\right) L/c_{\rm p}}{a_1(1-\phi^2)^2\left(\dfrac{2mc}{1+k-(1-k)\phi} - (T - T_{\rm m})\right)} \right\}. \tag{21}$$

This is the extreme restriction for the interface thickness. On the way approaching to this limitation the simulation results may be outside the regime of convergence because the negative driving force brings about artificial solute trapping effects. Anyway, the non-equilibrium effects relevant to the negative driving force are the prime reason for the extreme restriction and the interface thickness dependent simulation results.

4. Simulation and discussion

One-dimensional solidification into undercooled melts without kinetic effects is simulated with the same physical parameters as in Ref. [8],

$$\begin{aligned} &\frac{-m(1-k)}{L/c_{\rm p}} = 0.5325, \\ &\frac{T - T_{\rm m} - mc_\infty}{L/c_{\rm p}} = -0.55, \quad k = 0.15. \end{aligned} \tag{22}$$

Figure 2 shows $\partial_\phi f_{\rm mix}$ as a function of ϕ with different interface thicknesses at the evolution time $tD/d_0^2 = 83000$ with grid spacing $\mathrm{d}x = 0.4$. In Fig. 2(a), at a small interface thickness of $W/d_0 = 3.61$, $\partial_\phi f_{\rm mix}$ is positive in most regions across the diffuse interface. However, as shown in the inset, $\partial_\phi f_{\rm mix}$ is negative near the solid side of the interface in the magnified area. This consists with the previous analysis that $\partial_\phi f_{\rm mix} > 0$ cannot be satisfied across the whole diffuse interface during phase field simulation. With the increase of W/d_0, the negative phase transformation driving force becomes more obvious. As shown in Fig. 2(b), for a large interface thickness of $W/d_0 = 14.44$, the negative driving force is visible and there is an obvious minimum point on the curve of $\partial_\phi f_{\rm mix}$ at around $\phi = 0.5$. But in this case, the deviation is not strong enough to overcome the positive contribution of surface tension, which ensures the phase field can still evolve from liquid phase to solid phase ($\partial\phi/\partial t > 0$). During this kind of phase transformation the solid concentration will be higher than the equilibrium one, which is the so called solute trapping effect in the diffuse interface model. This kind of non-equilibrium may invalidate the simulation results. Further increase of W/d_0, i.e., the effect of surface tension cannot keep the mixture changing into solid phase. This causes the breakdown of the phase field profile, indicating the extreme limitation of interface thickness which is reached.

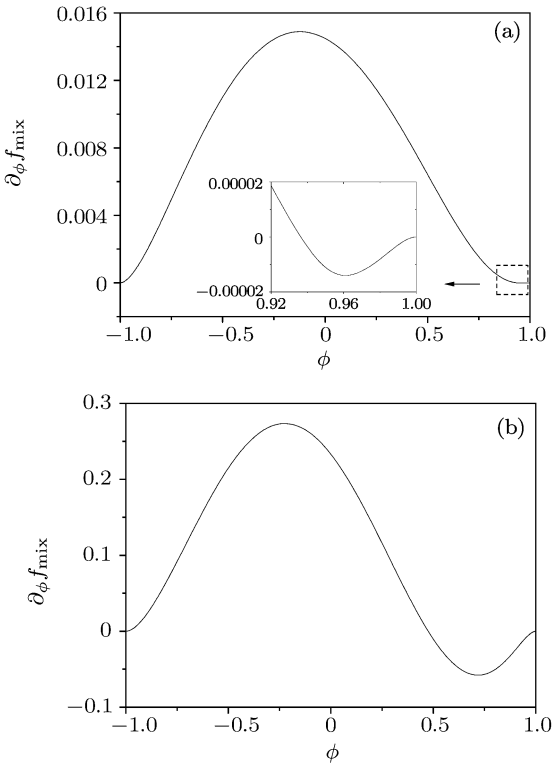


Fig. 2. The relevant thermodynamic driving force $\partial_\phi f_{\rm mix}$ at time of $tD/d_0^2 = 83000$, with grid spacing $\mathrm{d}x = 0.4$. (a) $W/d_0 = 3.61$, (b) $W/d_0 = 14.44$.

The diffuse interfaces from simulations with different interface thicknesses with a grid spacing $\mathrm{d}x = 0.4$ are shown in Fig. 3. At a small interface thickness, the phase field along the interface is close to the equilibrium distribution. Although the negative driving force is obvious for $W/d_0 = 14.44$, the diffuse interface is in a small deviation from the equilibrium shape. Therefore the thermodynamic driving force reflects the convergence limitation of interface thickness rather than the phase field variable. When the interface thickness exceeds a critical value, the interface breaks down on the side of solid phase region, which also happens even with much thinner grid spacing $\mathrm{d}x = 0.1$ as shown in Fig. 3(b). The simulation result

indicates that in the quantitative phase field model the inequality (19) at some certain local areas across the diffuse interface is caused by the intrinsic description of the phase field model. According to the above simulation results and analysis, it can be concluded that the non-equilibrium effects related to the negative driving force and the extreme limitation of the interface thickness, depending upon the non-equilibrium distribution of phase field profile and concentration profile, are intrinsic characteristic of the quantitative phase field model with diffuse interface. In inequality (21) the phase field and concentration distribution across the diffuse interface is very difficult to be obtained analytically. Evaluation and verification of the non-equilibrium effects can only be performed by numerical simulations. However, it is affected by simulation methodology because of the numerical-dependent phase field and concentration distribution.

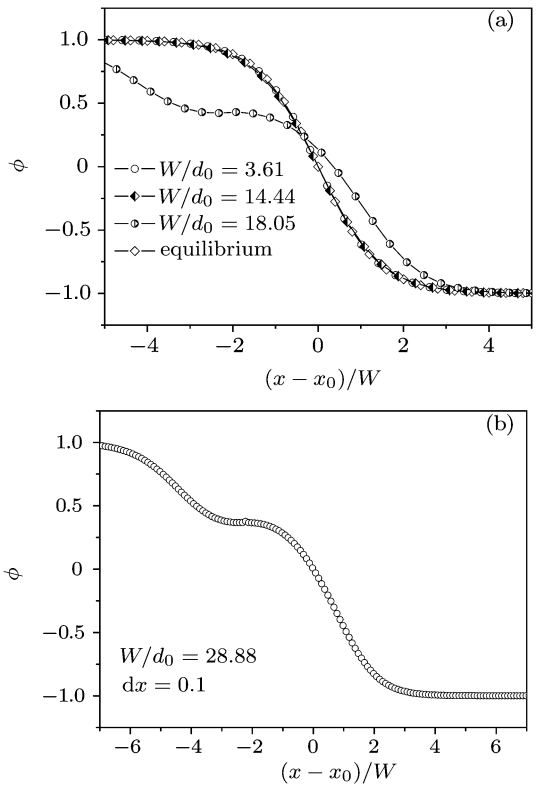


Fig. 3. The diffuse interface profiles with different interface thicknesses and grid spacing. The invalid interface shapes reveal that the interface thickness is beyond the upper limit.

Figure 4 shows the values of both sides of the inequality (21) at $dx = 0.4$ and $dx = 0.1$, respectively. The minimum value of the RHS of the inequality (21) exponentially decreases with the interface thickness. The crossing point corresponds to the extreme limitation of the interface thickness caused by the non-equilibrium effects. When the interface thickness is larger than the critical value, the inequality (21) is not satisfied.

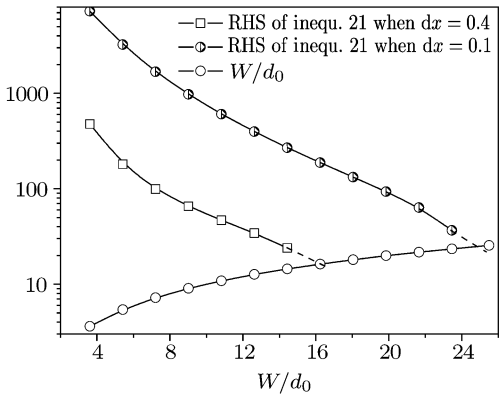


Fig. 4. Values of both sides of ineq. (21) with different W/d_0. The extension dash lines are drawn to give the crossing point approximately.

The discussion indicates that the phenomenon of $\partial\phi/\partial t < 0$ is inevitable in the phase field model, which cannot be eliminated by optimising the simulation methodology. The existence of negative driving force strongly interacts with the solute drag effect. Further understanding and characterising the negative area in Fig. 2 may uncover the quantitative description of solute drag effect in phase field model. Moreover, the requirement of simulation convergence on the interface thickness may be weaker by relaxing the extreme restriction on interface thickness. And the quantitative phase field may be amended to improve the simulation efficiency by releasing the non-equilibrium effects relevant to the negative driving force.

5. Conclusion

In summary, the non-equilibrium effects relevant to the negative driving force in the quantitative phase field model of binary alloys solidification have been presented. According to the analysis of phase transformation driving force, the existence of metastable solid phase in thermodynamics is uncovered during the simulation of solidification by the quantitative phase field model, which gives the thermodynamic explanation of the description of solute trapping effects in phase field model. For a larger interface thickness, the metastable solid phase may transits to liquid phase ($\partial\phi/\partial t < 0$), which destroys the process of phase transition. The extreme restriction of the interface thickness in the quantitative phase field model is demonstrated numerically according to the continuity of phase transition.

References

[1] Boettinger W J, Warren J A, Beckermann C and Karma A 2002 *Ann. Rev. Mater. Res.* **23** 163

[2] Li J J, Wang J C and Yang G C 2008 *Chin. Phys.* B **17** 3516

[3] Moelans N, Blanpain B and Wollants P 2008 *CALPHAD* **32** 268

[4] Wang Z J, Wang J C and Yang G C 2010 *Chin. Phys.* B **19** 017305

[5] Wang Z J, Wang J C and Yang G C 2009 *Phys. Rev.* E **80** 052603

[6] Karma A and Rappel A J 1998 *Phys. Rev.* E **57** 4323

[7] Karma A 2001 *Phys. Rev. Lett.* **87** 115701

[8] Ramirez J C, Beckermann C, Karma A and Diepers H J 2004 *Phys. Rev.* E **69** 051607

[9] Almgren R F 1999 *J. Appl. Math.* **59** 2086

[10] Wheeler A A, Boettinger W J and McFadden G B 1992 *Phys. Rev.* A **45** 7424

[11] Kim S G, Kim W T and Suzuki T 1998 *Phys. Rev.* E **58** 3316

[12] Qin R S and Wallach E R 2003 *Acta Mater.* **51** 6199

[13] Kim S G, Kim W T, Suzuki T and Ode M 2004 *J. Cryst. Growth* **261**135

[14] Ramirez J C and Beckermann C 2003 *41st AIAA Aerospace Sciences Meeting and Exhibit* AIAA 2003-816

[15] Hillert M and Rettenmayr M 2003 *Acta Mater.* **51** 2803