Liquid channel segregation and morphology and their relation with hot cracking susceptibility during columnar growth in binary alloys

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Abstract

The segregation and morphology of liquid channels at the last stage of solidification are closely related to hot cracking formation. We use Phase-Field (PF) simulations to investigate liquid channel characteristics during columnar growth of single-crystal and bi-crystal Al-Cu alloys. It is found that the back-diffusion is weak in Al-Cu alloys. Liquid channels in Al-2.0, 3.0wt%Cu alloys coalesce into droplets above the eutectic temperature while the reduced Hot Cracking Susceptibility of Al-4.0wt%Cu can be correlated to eutectic formation at the root of liquid channels. For bi-crystal growth, we demonstrate that non-equilibrium solute segregation at intergranular liquid channels (prospective Grain Boundaries (GBs)) depends on the convergent/divergent growth conditions between grains, and their misorientation angle. Divergent growth leads to stronger solute segregation as more solute diffuses laterally into divergent intergranular channels. It is thus expected that for the same GB energy, intergranular channels with higher solute composition can extend to lower temperatures, thus promote hot cracking. We introduce an approach for combining solid fraction vs. temperature curves calculated from microstructurally complex PF simulations with hot cracking models in the literature to predict the nominal composition with the highest HCS. Preliminary results from this work agrees well with experiments.

Keywords: Liquid channel, Segregation, Grain boundary, Phase-field, Hot cracking

1. Introduction

During columnar cellular/dendritic growth, the region where liquid and solid phases coexist due to segregation is termed as the mushy zone [1]. At the later stages of solidification, the microstructure forming inside the mushy zone is characterized by a dendritic solid skeleton with discontinuous liquid droplets and/or continuous channels distributed inside it. The liquid droplet and channels have quite different effects on the mechanical properties and hot cracking formation in the mushy zone. A solid network with liquid droplets behaves similarly to a coherent solid with slightly reduced strength and thus has a very low hot cracking susceptibility (HCS). A mushy zone with

wide liquid channels can avoid hot cracking by adjusting its morphology by liquid feeding. However, when the last liquid that exists is in the form of very thin liquid channels, an opening in the mushy zone cannot generally be compensated by liquid feeding, and hot cracking occurs [2]. It can be concluded that the liquid channel morphology at the last stage of solidification, especially thin regions at the roots of liquid channels and grain boundaries (GBs) is critical to hot cracking.

An extensive body of experimental work has shown that the HCS of an alloy strongly depends on its nominal composition, which exhibits the typical Λ -shape [2, 3]. The composition-dependent solidification interval (equilibrium or non-equilibrium) provides a convenient index to quantify HCS behaviour. Specifically, the larger the solidification range, the longer the liquid channel and the higher tendency of cracking. In the case of $k < 1$, where k is equilibrium partition coefficient

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cient, the solidification interval increases with the nominal composition initially and decreases after the formation of eutectics. The maximum freezing range thus corresponds approximately to the composition at which eutectics start to form. It is noted, however, that while eutectic reactions can take place in small liquid drops and liquid channels, it is the latter that are typically considered to have a strong effect on hot cracking formation.

Fig. 1 illustrates the trends on liquid channel morphology as a function of composition. For a dilute alloy containing only primary phase, solute segregation is weak and short liquid channels form (case a). Increasing the composition to a moderate value leads to stronger segregation and longer liquid channels with eutectic forming in isolated droplets (case b). Further increasing the nominal composition increases solute segregation further, leading to eutectic formation starting at the root of liquid channels (case c). Eutectic forming between two columnar dendrites (case c) is expected to prevent them from closing in on each other, leaving wider liquid channels that can facilitate liquid feeding and thus reduce the HCS. The distribution of metastable liquid below the eutectic temperature (T_e) is thus important to study in order to better understand hot cracking.

Normally, the length of liquid channels between the cells/dendrites can be characterized by the volume fraction of solid phase, $f_s(T)$, which in mean field theories is typically calculated by the Scheil equation. Here f_s is the volume fraction of solid phase and T is temperature. However, the Scheil equation can only examine volume fraction and not where dendrites coalesce. For this reason, coalescence is defined empirically to occur at $f_s = 0.94$ and the length of the liquid is usually determined to end at this point. The real image of where the columnar dendrites join each other is still poorly understood, particularly if the coalescence point is higher or lower than the eutectic temperature. Thus, a quantitative study that includes microstructural details about dendritic coalescence is important to show a real Λ relationship for HCS. The importance of a precise $f_s(T)$ predictor lies in that it is an input into models for predicting HCS, such as RDG model (Rappaz-Drezet-Gremaud).

In addition to the composition, another factor that can af-

fect the length of liquid channel is grain boundary angle. As discussed by Rappaz [4] the grain boundary can vary from attractive to repulsive with the variation of misorientation angle. A repulsive grain boundary [4] is believed to be a necessary condition to induce hot cracking by extending the intergranular liquid channel to temperatures lower than the coalescence temperature inside a single grain, T_b . In addition to the GB energy, non-equilibrium solute enrichment can also affect liquid channels and emerging GB structures. Namely, higher solute content leads to liquid channels that extend to lower temperatures, for a fixed GB misorientation energy, and thus have a higher HCS. Luo et al. [5, 6] have shown that solute segregation can make a material brittle by forming intergranular liquid channels. The role of GB energy and GB solute enrichment is convolved in alloys. To identify the effect of solute segregation alone, it would be instructive to examine large misorientation angles for which GB energy is approximately constant. It is generally expected that divergent and convergent growth will give different levels of non-equilibrium segregation at intergranular channels and resultant GBs.

Non-equilibrium morphological and segregation details inside the mushy zone and at GBs are thus quite important in providing an accurate $f_s(T)$ for the analysis of hot cracking formation. The Phase-Field (PF) method, with the advantage of avoiding interface tracking, has been widely used to modelling microstructure development [4, 7–10]. In addition, with the advent of accessible thin interface limit analyses coupled to parallel adaptive mesh refinement codes, the PF method has become a viable tool for handling large-scale simulations that can examine the development of the mushy zone in experimentally relevant systems for both single or polycrystalline columnar growth.

Using the Multi-Phase Field modelling approach, Böttger et al. have examined microstructure formation and its relationship with HCS during continuous casting of polycrystalline Low-Carbon and High-Strength Low-Alloyed Steels [11–13]. Their simulations show that micro-alloying such as Ti and related precipitates have a pronounced effect on HCS by increasing the

coalescence temperature.

This work uses a recent quantitative Multi-Order Parameter phase field model of alloy solidification to study HCS in solidification under laser welding conditions in the Al-Cu system, with the aim of isolating and characterizing the specific roles of solute on coalescence and eutectic formation in single crystal and bi-crystal columnar growth, as well as non-equilibrium segregation effects on the coalescence of bi-crystal grain boundaries. In the case of single crystal directional solidification, the effect of the nominal composition on liquid channel segregation and morphology is examined, and the results using the Scheil equation are compared to from PF simulations. In the case of bi-crystal directional solidification, the dependence of intergranular solute enrichment on convergent/divergent growth conditions and mis-orientation angle are characterized. Finally, we also couple analysis from our phase field simulations to the RDG and Kou models of hot cracking to specifically identify the nominal composition corresponding to the highest HCS in Al-Cu alloys. Our results demonstrate that the effect of the nominal composition, divergent/convergent growth conditions and misorientation angle between bi-crystals, can have a significant effect on solute segregation and, thus, hot cracking formation in welding processes.

2. Phase Field Model of Polycrystalline Solidification

To investigate solute segregation at liquid channels and emerging GBs, the quantitative multi-order parameter PF model of polycrystalline binary alloys developed by Ofori-Opoku et al. [14] was used. In the model, c represents solute concentration and T is the temperature. Each grain, i , is represented by an order parameter ϕ_i , which tracks the solid-liquid interface of a given grain. Nominally, each $\phi_i = 1$ in the bulk of the i^{th} grain, while $\phi_i = 0$ in the liquid or in the bulk of any other grain, $j \neq i$. The interactions between order parameters are defined such that $\phi_1 + \phi_2 + \dots + \phi_N < 1$ everywhere. (Practically, we work with interpolation functions that allow ϕ_i to vary between $-1 < \phi_i < 1$). Ordering in the system is completely defined everywhere by the set $\{\phi_i\}$, which is compactly represented by

a phase field vector $\vec{\phi} = (\phi_1, \phi_2, \dots, \phi_N)$, where N is the total number of grains in the system.

2.0.1. Free energy functional

In terms of c , $\{\phi_i\}$ and T , the free energy functional of a solidifying alloy is

$$F(\vec{\phi}, c, T) = \int d\mathbf{x}^3 \left\{ \frac{1}{2} \sum_i |\epsilon(\vec{\phi}) \vec{\nabla} \phi_i|^2 + f(\vec{\phi}, c, T) + f_{int}(\vec{\phi}) \right\}, \quad (1)$$

where $\mathbf{x}$ is a spatial variable. Here, $f_{int}(\vec{\phi})$ controls the interaction between the ϕ_i and prevents overlap in the bulk of grains. Its form is given by

$$f_{int}(\vec{\phi}) = \sum_i \sum_{j \neq i} \alpha_{ij} \left(\frac{1 + \phi_i}{2} \right)^2 \left(\frac{1 + \phi_j}{2} \right)^2, \quad (2)$$

where α_{ij} is an energy density, set here to a constant ($\alpha_{ij} = \alpha$). The remainder of the bulk free energy follows the form

$$f(\vec{\phi}, c, T) = H f_D(\vec{\phi}) + f_{id}(\vec{\phi}, c, T) \quad (3)$$

where $f_D(\vec{\phi}) = \sum_i (-\phi_i^2/2 + \phi_i^2/4)$ sets a barrier between each ϕ_i and the liquid, and H defines a nucleation barrier energy scale ($[H] = \text{J/m}^3$). The function $f_{id}(\vec{\phi}, c, T)$ is the standard free energy of an ideal binary alloy, written explicitly in polycrystalline form in Ref. [14]. The function $\epsilon(\vec{\phi})$ in Eq. (1) is a gradient energy coefficient ($[\epsilon^2] = \text{J/m}$) that is modulated by the value of the order parameter set $\{\phi_i\}$ to take on different values for solid-liquid and solid-solid interfaces.

The dynamics of the order parameter ϕ_i are defined through the minimization of the functional in Eq. (1), namely $\partial \phi_i / \partial t = -M \delta F / \delta \phi_i$, where M is a mobility governing the order pa-

parameter kinetics. In expanded form this equation becomes

$$\begin{aligned} \tau(T) \frac{\partial \phi_i}{\partial t} = & \vec{\nabla} \cdot \left(W(\vec{\phi})^2 \vec{\nabla} \phi_i \right) \\ & + \partial_x \left(|\vec{\nabla} \phi_i|^2 W(\vec{\phi}) \frac{\partial W(\vec{\phi})}{\partial (\partial_x \phi_i)} \right) \\ & + \partial_y \left(|\vec{\nabla} \phi_i|^2 W(\vec{\phi}) \frac{\partial W(\vec{\phi})}{\partial (\partial_y \phi_i)} \right) \\ & + \phi_i - \phi_i^3 \\ & - \bar{\lambda} (1 - \phi_i^2)^2 \left(U + \frac{T - T_0}{|m|(1 - k)c_l^0} \right) \\ & - \omega \frac{1 + \phi_i}{2} \sum_{j \neq i} \left(\frac{1 + \phi_j}{2} \right)^2, \end{aligned} \quad (4)$$

where $W(\vec{\phi}) = \epsilon(\vec{\phi})/\sqrt{H} = W_0 a(\vec{\phi})$, with W_0 the characteristic length of the solid-liquid interface and $a(\vec{\phi})$ a dimensionless gradient energy function, while $\bar{\lambda} = RT(1 - k)^2 c_l^0 / (\Omega_o H)$, $\omega = \alpha/H$, and $(T_0, c_l^0, m, k, \Omega_o)$ are, respectively, a reference temperature, the solute composition on the liquid side of a steady-state planar interface at T_0 , the liquidus slope, the solute partition coefficient of the alloy, and the molar volume of the material. Also, t is time and $\tau(T) = \tau_o \bar{\tau}(T)$, where, following Ref. [15],

$$\bar{\tau}(T) = \left[1 - \frac{T - T_0}{|m|c_l^0} \right] a^2(\vec{\phi}), \quad (5)$$

and τ_o sets a kinetic time scale defining fluctuations in ϕ_i . The supersaturation field U defined by

$$U = \frac{1}{1 - k} \left\{ \frac{2c/c_l^0}{1 + k - (1 - k) \sum_i \phi_i} - 1 \right\} \quad (6)$$

Here, the constant $\bar{\lambda}$ couples ϕ_i to U , and is considered a convergence parameter to achieve correspondence with sharp interface kinetics.

The dynamics of the supersaturation U are governed by

$$\begin{aligned} \left(\frac{1 + k}{2} - \frac{1 - k}{2} \phi \right) \frac{\partial U}{\partial t} = & \vec{\nabla} \cdot \left(D_l q(\vec{\phi}) \vec{\nabla} U - \vec{j}_{at} \right) \\ & + [1 + (1 - k)U] \frac{1}{2} \sum_i \frac{\partial \phi_i}{\partial t}, \end{aligned} \quad (7)$$

where $q(\vec{\phi})$ modulates solute diffusion across interfaces. Its

form is given by

$$q(\vec{\phi}) = \frac{1 - \psi}{2} + \frac{(1 + \psi)[1 + k + (1 - k)\psi]}{4} \frac{D_s}{D_l}, \quad (8)$$

where $\psi = \sum_i \phi_i + (N - 1)$, and D_l , and D_s liquid diffusion coefficient, and solid diffusion coefficient, respectively. The term $\vec{j}_{at}$ is a non-variational term called the anti-trapping flux. It is added in as part of a strategy for the any solid-liquid interface defined by ϕ_i to emulate the sharp-interface model for alloy solidification in the limit of diffuse interfaces. Its form was generalized from Ref. [15] to

$$\vec{j}_{at} = -\frac{1}{2\sqrt{2}} [1 + (1 - k)U] \sum_i \frac{\partial \phi_i}{\partial t} \frac{\vec{\nabla} \phi_i}{\vec{\nabla} \phi_i} \quad (9)$$

The term $\vec{j}_{at}$ becomes negligible for solid-solid interfaces and at vanishing solidification rates. It is noted that the concentration c_l^0 is related to the nominal composition of the binary alloy, c_0 , by $c_l^0 = c_0/k$.

Temperature is modelled in the phase field simulations by a frozen temperature approximation corresponding to Bridgman directional solidification. Its form is given by

$$T(y, t) = T_0 + G(y - V_p t), \quad (10)$$

where G is the thermal gradient and V_p is the pulling velocity.

All calculations with the above model, and results shown, assume that space and time are dimensionless through the rescaling $x \rightarrow x/W_0$ and $t \rightarrow t/\tau_o$, respectively. The relationship between the parameters W_0 , τ_o and $\bar{\lambda}$ is discussed further below. Our simulations were carried out in 2 dimensions.

2.1. Modeling solid-liquid interfaces

The PF model parameters (W_0, τ_o) are selected such that the kinetics of any free solid-liquid interface defined by any ϕ_i reproduce the boundary conditions of the sharp-interface solidification model, in the limit of diffuse interfaces [15]. Namely, (W_0, τ_o) are chosen such that the isotropic components of the chemical capillary length, d_0 , and the interface kinetic coefficient,

cient, β , are related to the PF parameters by

$$d_0 = \frac{\Gamma}{(|m|(1-k)c_l^0)} = \frac{a_1 W_0}{\bar{\lambda}} \quad (11)$$

$$\beta = \frac{a_1 \tau_0}{\bar{\lambda} W_0} \left[1 - a_2 \frac{\bar{\lambda} W_0^2}{\tau_0 D_l} \right], \quad (12)$$

where $a_1 = 5\sqrt{2}/8$, $a_2 = 0.6267$, and Γ is the Gibbs-Thompson coefficient. In this approach, $\bar{\lambda}$ plays the role of a convergence parameter. Once set, it specifies, for a specific material, W_0 and τ_0 through Eqs. (11) and (12). In this work, we set τ_0 through the relation $D_l \tau_0 / W_0^2 = a_2 \bar{\lambda}$, which effectively makes $\beta = 0$ at in simulations. We used $\bar{\lambda} = 10$ at solid-liquid interfaces in our simulations. At the cooling rates examined, this value is small enough to map the dynamics of solid-liquid interfaces defined by ϕ_i onto the corresponding sharp interface model for alloy solidification, defined by d_0 and β [9, 10, 16].

The anisotropy of the solid-liquid interface energy is modelled through the function $a(\vec{\phi})$, which becomes

$$a(\vec{\phi}) \rightarrow \mathcal{A}(\psi) = a_s \left(1 + \frac{4\epsilon_4}{a_s} [\cos^4(\psi) + \sin^4(\psi)] \right) \quad (13)$$

along any solid-liquid interface defined by any ϕ_i , where $a_s = 1 - 3\epsilon_4$ and ψ is the angle of the interface normal of each grain with the x-axis. The small parameter ϵ_4 is the anisotropy strength. To interpolate the function $a(\vec{\phi})$ continuously between its form in Eq. (13) and its form at solid-solid interfaces (see below), the parameter $\mathcal{E} = (\phi_i + 1)^2 \sum_{j \neq i} (\phi_j + 1)^2$ is used. In particular, if $\mathcal{E} < \epsilon'$ (ϵ' is a small number) at any point of any ϕ_i , Eq. (13) is applied, otherwise $\mathcal{E} \geq \epsilon'$ corresponds to solid-solid interface between ϕ_i and one or more ϕ_j , $j \neq i$.

2.2. Modeling grain boundaries

When updating the equation of motion for any ϕ_i , if the criterion $\mathcal{E} \geq \epsilon'$ (see previous section) is satisfied for any position and any $j \in \{1, 2, \dots, N\}$, this is taken to correspond to a solid-solid interface between grain i and grain j . When $\vec{\phi}_i$ satisfies the above condition along any i - j interface, the dimensionless gradient energy coefficient becomes

sionless gradient energy coefficient becomes

$$a(\vec{\phi}) \rightarrow M[\vartheta_{ij}/\theta_m] [1 - \ln(\vartheta_{ij}/\theta_m)] \mathcal{A}(\psi) \quad (14)$$

where ϑ_{ij} denotes the misorientation angle between grain i and grain j , and M is a dimensionless scaling factor, set to $M = 1$ in this work. θ_m is the angle at which GB energy reaches a maximum. Equation (14) describes the Read-Shockley grain boundary energy form [17]. For practicality, the function

$$\theta(\vec{\phi}) = \frac{\sum_{ij} \vartheta_{ij} (\phi_i + 1)^2 (\phi_j + 1)^2}{\sum_{ij} (\phi_i + 1)^2 (\phi_j + 1)^2} \quad (15)$$

is used to calculate mis-orientation angle locally in $a(\vec{\phi})$.

For a grain boundary defined by two order parameters, ϕ_i and ϕ_j , the interface energy, γ_{gb} , is determined by

$$\begin{aligned} \gamma_{gb}(\theta) = H W_0 \int_{-\infty}^{\infty} \left[\frac{1}{2} \sum_i a^2(\vec{\phi}) \left(\frac{d\phi_0^i}{d\xi} \right)^2 + \sum_{i=1}^2 f_D(\phi_0^i) \right. \\ \left. + 2\omega \left(\frac{\phi_0^i + 1}{2} \right)^2 \left(\frac{\phi_0^j + 1}{2} \right)^2 - f_D^{\text{bulk}} \right] d\xi, \end{aligned} \quad (16)$$

where $a(\vec{\phi})$ is given by Eq. (14), $\xi = x/W_0$ and (ϕ_i^o, ϕ_j^o) correspond to the steady state solutions of the phase field equations of an i - j bi-crystal in 1D, which can be computed numerically [14]. Since the results presented here are not sensitive to the precise value of γ_{gb} , the functions ϕ_i^o and ϕ_j^o are taken, for simplicity, as the usual hyperbolic tangent profile solutions. When $\theta = \theta_m$, $a(\vec{\phi}) = \mathcal{A}(\psi)$, yielding the maximum grain boundary energy, denoted $\gamma_{gb}(\theta_m) = \gamma_{gb}^{max}$. The solid-liquid interface energy is given by $\gamma_{sl} = a_1 H W_0$. Thus, Eq. (16) scales the GB energy by the corresponding solid-liquid surface energy defined by $W_0 H$.

The interaction ω can be set under the assumption of negligible equilibrium adsorption at a steady-state solid-solid interface. Following Ref. [14], this is achieved by setting $\omega = A\bar{\lambda}(T - T_s)/(T_s - T_l)$, where A is a proportionality constant, determined numerically here to be $A \approx 8$. Note that the GB adsorption mentioned here is the composition difference of GBs

from bulk composition at equilibrium. Kinetic processes such as solidification and grain growth can also cause composition differences which is referred to as non-equilibrium segregation/enrichment [18].

The considerations above reveal that the ratio $\gamma_{gb}(\theta)/\gamma_{sl}$ depends on the *driving force coefficient* $\Delta \equiv \bar{\lambda}(T - T_s)/(T_s - T_l)$. The dependence of $\gamma_{gb}^{\max}$ on Δ and $\gamma(\theta)$ vs. θ , for a particular Δ , were calculated numerically and are shown in Fig. 2(a) and (b), respectively. In the simulations reported here, we set $\bar{\lambda} = 0.2$ along any solid-solid interface, and calculated $\gamma^{\max}$ based on the temperature $T = 750$ K. For this choice of $\bar{\lambda}$, this corresponds to a grain boundary energy many times larger than the solid-liquid energy, which was assumed for simplicity. Different grain boundary energies can be attained by tuning the A , $\bar{\lambda}$ and T . It is noted also, that attractive and repulsive grain boundaries can be modelled by varying the misorientation (Fig. 2(b)).

2.3. Implementing noise in simulations

Compositional fluctuations induced by thermal noise are included in simulations by adding a stochastic mass flux to U evolution equation (Eq. (7)), the statistics of which satisfy

$$\langle J_u^m(\vec{r}, t) J_u^m(\vec{r}', t) \rangle = 2Dq(\phi) F_u \delta(\vec{r} - \vec{r}') \delta(t - t') \quad (17)$$

Following Ref. [19], the magnitude of the fluctuations is given by $F_u = F_u^0[1 + (1 - k)U]$, where $F_u^0 = k\Omega_0/(1 - k)^2 N_A C_0$, N_A is Avogadro's number and Ω_0 is molar volume of solvent atoms. In numerical simulations, noise amplitude is scaled with the grid spacing. Details of the noise implementation can be found in [19]. It is found that the simulation microstructures are mainly cellular even with noise included, which is experimentally consistent [20]. This can be attributed to small primary spacing due to high growth velocity and thermal gradient. For divergent growth, the space between two grains also adopts side-branches.

2.4. Material, solidification conditions

The well-characterized Al-Cu alloy system was selected in this work with the physical properties listed in Table 1. The liquidus and solidus are nearly straight lines with m and k nearly constant. Nominal compositions of 2.0, 3.0, and 4.0wt%Cu were studied. We used a thermal gradient $G = 1 \times 10^6$ K/m and an isotherm velocity $V_p = 5$ mm/s, which are typical solidification conditions in lower speed laser/electron beam welding processes. For metals and non-faceted alloys, interface non-equilibrium effects typically become important when the growth velocity is greater than 10 mm/s. Therefore, the atomic attachment effect and solute trapping effect are neglected here. For all calculations, the minimum grid spacing $dx/W_0 = 0.8$ was used and the total system size is 180 μm in growth direction and 108 μm in width direction. The phase-field equations are solved with a finite difference method implemented on an adaptive mesh refinement algorithm analogous to the original version by Provatas et al. [21, 22].

3. Results

Fig. 3 shows liquid channel morphologies during columnar growth of Al-2.0, 3.0, and 4.0wt%Cu alloys under the same solidification conditions, with four isotherms at temperatures T_m (melting), T_l (liquidus), T_s (solidus), and T_e (eutectic) indicated. The microstructures appear to be cellular in most cases. As with the primary spacing, there is a variability in liquid channel length. When only the primary reaction is considered, the length of liquid channels increases with increasing nominal composition from 2.0% to 4.0wt%Cu. However the liquid below T_e becomes metastable and will transform to eutectic. In this work, we assume this metastable liquid $\rightarrow$ eutectic reaction can occur fairly close to T_e and in a short time scale. Therefore, the metastable liquid can be approximately regarded as the reverse of non-equilibrium eutectic phase.

The solid fraction vs. temperature, $f_s(T)$ curves calculated from PF simulations and from the Scheil equation for Al-2.0, 3.0, and 4.0wt%Cu alloys are shown in Fig. 4. Both PF simulations and the Scheil equation predict the similar trend with

nominal composition and agree well with each other at low f_s range. At high f_s , PF simulations give higher $f_s(T)$ for given temperature, predicting the end of primary solidification at higher temperatures (e.g. Al-2.0wt%Cu), and a lower fraction of non-equilibrium eutectics (e.g. Al-3.0, 4.0wt%Cu).

Fig. 5 shows the $f_s(T)$ curves for Al-3.0wt%Cu alloys from PF simulations with different solid diffusion coefficients. The solid diffusion is seen to have a strong effect on $f_s(T)$ at high f_s range and at low temperature. The difference between $D_s = 0$ and $3.0 \times 10^{-13} \text{ m}^2/\text{s}$ is minimal. With the increase of solid diffusion coefficient from 3.0×10^{-13} to $3.0 \times 10^{-11} \text{ m}^2/\text{s}$, back-diffusion affects the $f_s(T)$ curve substantially.

Fig. 6 shows the liquid channel morphologies in columnar growth of a diverging bi-crystal in Al-2.0wt%Cu and Al-4.0wt%Cu alloys. The divergent bi-crystals have a misorientation angle of 20° . Regions just below T_e are enlarged to show structural details of the liquid pools. The intergranular liquid channel in the Al-2.0wt%Cu alloy merges above T_e and forms a continuous GB. In the Al-4.0wt%Cu alloy, metastable liquid exists below T_e , and only part of intergranular channel starts to overlap.

The solute distribution maps for convergent and divergent growth of Al-2.0wt%Cu bi-crystals is presented in Fig. 7. For the same misorientation, the divergent growth leads to higher solute composition in the intergranular liquid channels compared to convergent growth. The dependence of this non-equilibrium solute segregation at GBs versus misorientation is plotted in Fig. 8 for the data of Fig. 7. We defined grain boundaries as areas in the data where the two order-parameter fields start to overlap, based on the criterion discussed in the model section. Segregation is seen to increase with misorientation for converging growth conditions, while it decreases with misorientation for divergent growth conditions.

4. Discussion

4.1. Liquid channels in single crystal columnar growth

The segregation in liquid channels can be influenced strongly by the alloy nominal composition. For a given alloy with

constant solute partition coefficient, k , solute segregation increases with the nominal composition. Increasing the nominal composition gives rise to inter-dendritic/cellular liquid channels which contain more solute and can remain stable at lower temperatures. This can be seen in Fig. 3. One way to describe segregation in liquid channels is through $f_s(T)$, which can be calculated from either microsegregation models or PF simulations. When the temperature is below T_e , any remaining liquid becomes metastable and will transform to eutectic phase. Assuming eutectic reaction happens close to T_e and back-diffusion is weak, the fraction of eutectic can be approximated by $f_e = 1 - f_s(T_e)$. $f_s(T)$ curves can also be calculated from the Scheil equation. Several approximations are made in this formalism, namely, zero back-diffusion, infinitely rapid liquid diffusion, and planar solid-liquid interface. In terms of the nominal composition effect on segregation, the Scheil equation predicts similar results as PF simulations at small f_s . However, the Scheil equation predicts higher liquid fraction (f_l) in the high f_s range (Fig. 4). A possible reason for this discrepancy can be due to the fact back-diffusion is neglected in the Scheil equation, which modifies $f_s(T)$ by reducing solute segregation in the liquid.

To further examine the role of back-diffusion effect on $f_s(T)$, PF simulations with different solid-diffusion coefficient, D_s are performed and the result is shown in Fig. 5. Increasing the solid state diffusion coefficient increases the back-diffusion substantially, with the difference between the curves becoming larger with undercooling below T_s . For Al-Cu alloys considered here, $D_s \approx 3.0 \times 10^{-13} \text{ m}^2/\text{s}$ and back-diffusion has a minimal effect on $f_s(T)$, as in the Scheil model with $D_s = 0$. However, other Al alloys such as Al-Mg and Al-Zn have a much lower T_e , above which the liquid can remain stable. In those cases, the driving force for back-diffusion can be large and affect $f_s(T)$ curves substantially assuming constant D_s [4, 14]. Therefore, back-diffusion needs to be considered when studying the HCS of alloys with low T_e [23, 24]. In this work, the main reason for the difference in $f_s(T)$ between the Scheil equation and PF simulations can be attributed to the variability of liquid channel

lengths and interface curvatures, which makes the PF composition at interfaces inside channels deviate from the equilibrium composition of phase diagram and thus affect $f_s(T)$.

In addition to $f_s(T)$, it is also important to consider the spatial morphology and distribution of liquid. One feature of importance in this case would be the value of the eutectic temperature, T_e relative to the coalescence temperature, T_b . Liquid below T_e is metastable and transforms to eutectic phase. This can happen over a short time scale and can change the liquid morphology substantially. Otherwise the liquid channels can coalesce into isolated droplets at T_b . Therefore the metastable liquid can be either inside liquid channels or in the form of droplets, depending on the relative values of T_b and T_e [25]. When $T_b > T_e$ (Al-3.0wt%Cu), thin liquid channels typically transform to liquid droplets first and the eutectic reaction takes place inside these droplets. For Al-4.0wt%Cu, $T_b < T_e$, which implies that metastable liquid $\rightarrow$ eutectic reaction will predominantly take place inside liquid channels. **In this case, eutectics can form continuously and a so-called "continuous eutectic" can be observed. This is shown by Liu et al. very recently [26] in welds of 2014 Al (an alloy with compositions close to 4.0wt%Cu).** This is consistent with Fig. 3(c), in which wider liquid channels in Al-4.0wt%Cu will form eutectic phases between the two columnar dendrites and prevent the formation of thin liquid channels, thus permitting liquid feeding, which decreases HCS. Reduced HCS of Al-4.0%Cu alloys has been observed experimentally. Katgerman et al. [27, 28] studied the effect of composition on hot cracking during chill casting of Al-Cu alloys, also observing no hot cracking for alloys with Cu content higher than 4.0.

4.2. Intergranular liquid channels in bi-crystal growth

Hot cracking is normally observed at GBs. The GB effect on hot cracking can be explained by repulsive GBs extending intergranular liquid channels to much lower temperatures than T_b . The energy of tilted GB, γ_{gb} increases with misorientation, reaching the maximum value at $\theta = \theta_m$ and remaining constant (Fig. 2(b)). During the merger of intergranular liquid channels,

two solid-liquid interfaces are replaced by one GB. For small-angle GBs, $\gamma_{gb} < 2\gamma_{sl}$, and there is a free energy decrease in formation of a GB, favouring intergranular liquid channel merger at $T = T_b$, the same temperature as for liquid channels in a single grain. For large misorientation, $\gamma_{gb} > 2\gamma_{sl}$, and a larger undercooling is required to provide a driving force for GB merger. This undercooling is given by

$$\Delta T_b(\theta) = \frac{\gamma_{gb}(\theta) - 2\gamma_{sl}}{\Delta S_f \delta}, \quad (18)$$

where ΔS_f is the volumetric entropy of fusion and δ is the width of solid-liquid interface. δ is not well-defined but is on the order of nanometers. In this work, we only consider high-angle GBs and $\Delta T_b = \Delta T_b(\theta_m)$ will be used hereafter. The specific value of ΔT_b is material-dependent. However, this value is believed to be large for alloys. $\Delta T_b = 83$ K is predicted for MC2 superalloys, as shown by Wang et al. [29]. More recently, by using High-resolution transmission electron microscopy and Auger spectroscopy, Luo et al. [5] observed nano-scale liquid layers at 95 K below the bulk eutectic temperature. $\Delta T_b = 48$ K can be estimated for Al-Cu alloys when $\gamma_{gb} = 2.2\gamma_{sl}$ and $\delta = 1$ nm are used. This undercooling is large enough to extend the intergranular liquid channels in Al-3.0,4.0wt%Cu alloys below T_e , i.e. $T_b - \Delta T_b < T_e$. A large ΔT_b implies that high-angle GBs can remain wet at the temperature between T_b and $T_b - \Delta T_b$, a temperature range where most liquid regions have solidified. This thin GB liquid layer can reduce the strength and is hard for liquid feeding, which makes $T_b - \Delta T_b < T < T_b$ the most vulnerable range to form hot cracking. It is instructive here to distinguish full liquid structure (blue color in Fig. 6) from the nano-scale liquid layers formed at wet GBs, which are considered to be partially-ordered (yellow color) "liquid-like" structure [5]. We will refer this "liquid like" structure as GB liquid layer.

While the lowest temperature at which GBs can remain wet is $T_b - \Delta T_b$, whether or not the intergranular liquid channel can extend to this lowest temperature depends on the structure formed between two grains. This point can be illustrated

clearly in Fig. 6. In the Al-2.0wt%Cu alloys (Fig. 6(a)), where intergranular channels start to merge to form wet GB for temperatures above T_e , which can stay wet until $T_b - \Delta T_b$. In contrast, in the Al-4.0wt%Cu alloy the liquid contains more solute which leads to more metastable liquid and only parts of the liquid channels merge and form wet GBs, as demonstrated in Fig. 6(b). Since for Al-4.0wt%Cu, $T_b - \Delta T_b < T_e$, the metastable liquid is thus expected to form eutectic phase and thus interphase boundaries. Therefore, the liquid layer formed in this case cannot continuously extend to $T_b - \Delta T_b$ as it will be interrupted by interphase boundaries. In principle, the interphase boundaries have extra energy and can remain wet to certain temperatures as long as their energy is larger than $2\gamma_{sl}$. However, for the Al-Al₂Cu eutectics expected to form in this system, experimental studies [30] show that low-energy semi-coherent interphase boundaries form, which is not expected to stay wet to the lowest temperature $T_b - \Delta T_b$. It can be inferred that compared to the high-angle GB, interphase boundaries in this case are less likely to promote hot cracking.

Solute segregation at emerging GBs depends strongly on the configuration of solidifying grains (divergent or convergent growth), as well as the misorientation angles. For small angle misorientations, GB segregation and misorientation energy are coupled. To isolate the effect of segregation alone, high-angle GBs, with energy independent of misorientation were considered in PF simulations. The results are shown in Figs. 7 and 8. It was found that divergent growth always leads to higher solute segregation at intergranular channels than convergent growth. This difference can be explained by the lateral diffusion in liquid ahead of dendrite arrays. For convergent dendrites which grow towards each other, there is a strong solute interaction and a higher solute pile-up in front of tips, which leads to diffusion in the lateral direction away from the space between the grains. In contrast, divergent primary dendrite stems grow away from each other, leaving the area between them less saturated with impurities. This creates a mass sink for solute to diffuse into the space between the dendrites.

Both the convergent and divergent bi-crystal growth cases are

also found to be modulated by misorientation angle (Figs. 7 and 8). The solute field in front of two divergent/convergent dendrites can also depend on orientation-dependent primary spacing and side-branch growth for divergent cases. This makes the dependence on misorientation complicated. It is plausible, for example, that more side-branches developed with the increasing divergent angle prevent solutes from going further into the space between dendrites and thus GB segregation decreases.

The data discussed above from our PF simulations suggests that convergent growth conditions lead to lower solute segregation at GBs. For the same GB misorientation, liquid at GBs with higher solute has a lower energy, and can remain stable to lower temperatures. It is expected that short liquid channels will form in this case, which leads to a reduced HCS. This prediction suggests a plausible mechanism for avoiding cracking when welding two components with highly different misorientations, which needs to be verified experimentally in the future.

The width of liquid channels at GBs is on the same scale as the solid-liquid interface width. As diffuse interfaces are required to perform large scale PF simulations, it is only possible to resolve the liquid layers at GBs qualitatively below this length, since the physical structure of a liquid channel cannot be modelled at the atomic scale [31]. Nevertheless, the PF simulation can still be used to characterize the magnitude of segregation over a wide range of GB sizes and misorientations, as well as to characterize the length and morphology of extended liquid channels at GBs. PF calculations of such properties can then be used to diagnose HCS in many alloy systems. A proposed future direction for further research is the combination of PF and phase field crystal (PFC) modelling to examine the role of atomic-scale structure on GB energy and segregation, and to predict liquid channel length and morphology at GBs [32–34]. The non-equilibrium segregation and channel morphologies during solidification occupy microstructural length scales, which can be simulated using the PF method. PFC can then use information gathered from PF simulations to examine GB interfaces, at the microscopic scale and on diffusive time scales [35, 36].

4.3. Combining hot cracking models with PF Simulations

This section develops a methodology to combine information from phase field simulations with the the RGD and Kou models to identify the composition with the highest HCS in directional solidification. The occurrence of hot cracking is caused by the combined effect of tensile stress and solidification shrinkage. Considering columnar growth in one direction with tensile deformation perpendicular to growth direction and liquid feeding opposite to the growth direction, the RGD model predicts the pressure drop along a liquid channel given by

$$\begin{aligned}\Delta p_{max} &= \Delta p_e + \Delta p_{sh} \\ &= \frac{180}{\lambda_i^2} \frac{(1 + \beta)\mu}{G} \int_{T_S}^{T_L} \frac{E f_s^2}{(1 - f_s)^3} dT \\ &\quad + \frac{180}{\lambda_i^2} \frac{v_T \beta \mu}{G} \int_{T_S}^{T_L} \frac{f_s^2}{(1 - f_s)^2} dT,\end{aligned}\quad (19)$$

where T_L , T_S are the liquidus temperatures at the tips of the dendritic array and the temperature at the roots of the liquid channels, respectively. $E(T)$ is given by

$$E(T) = \frac{1}{G} \int f_s(T) \dot{\epsilon}_p(T) dT, \quad (20)$$

where μ is the liquid viscosity, β the shrinkage factor, G the thermal gradient, and v_T velocity of isotherms. λ_i is the microstructural length scale, with $i = 1$ corresponding to the primary spacing for cellular growth and $i = 2$ to secondary spacing for dendritic growth. $\dot{\epsilon}_p$ is the deformation rate of the solid perpendicular to the growth direction. Based on the similar physics as the RGD model, Kou proposed, instead of pressure drop, using the maximum of the simple index $|dT/d\sqrt{f_s}|$ [37] to characterize HCS. **We examine both models here.**

As analytical models, the RGD and Kou models have two limitations. The first is that these models are sensitive to the $f_s(T)$ information used. As shown in [23], with the increase of back-diffusion and thus variation in $f_s(T)$, the HCS peak shifts to higher solute contents. The back-diffusion coefficient, however, is not easy to determine as its value depends on cooling rate, microstructure scale and solid diffusion coefficient. Moreover, mean field type models such as those in Eq. (19) do not

account for channel length and width variability. In this work we use $f_s(T)$ curves calculated from PF simulations, which implicitly incorporates the dependence of back diffusion and microstructure variability statistics along each isotherm.

A second limitation is that the solidification temperature at the roots of liquid channels, T_S , is not well-defined and its selection can change the Λ curve. This temperature enters the RGD model as the lower limit of the integral in Eq. (19), and in the Kou model $|dT/d\sqrt{f_s}|$ reaches its maximum at T_S . In the original RGD paper, T_S is defined as $T(f_s = 0.98)$ if eutectic fraction is less than 2%, or T_e otherwise. In this case, the maximum HCS is predicted to be 1.4wt%Cu. A similar result of 1.5wt%Cu is predicted by Kou with T_S defined by where $\sqrt{f_s} = 0.99$ [37]. Those predictions are close to 1.0wt%Cu observed in casting experiments [38, 39]. However, Most welding experiments observed the peak around 3.0wt%Cu [40–42].

To determine T_S from our PF simulation data, we proceed as follows. Referring to Fig. (3), we first determine the liquid fraction at a specific vertical height (T -isotherm) by rastering horizontally, and integrating the total area of liquid ($\phi = -1$). We denote that liquid fraction by f_l^{channel} . The solid fraction at that temperature is then given by $f_s^{\text{channel}} = 1 - f_l^{\text{channel}}$. It is noted that in this part of the calculation, liquid droplets and metastable liquid are taken as solid. $f_s^{\text{channel}}(T_S) \rightarrow 1$ determines the temperature T_S . If $f_s^{\text{channel}} \rightarrow 1$ below T_e , then T_S is set to T_e . Once T_S is thus established based on the above assumptions, we evaluate Eq. (19), using the actual $f_s = 1 - f_l$ into the integrand, where f_l is calculated by integrating the total liquid fraction at each isotherm.

Fig. 9 plots the pressure drop calculated Eq. (19), for the Al-2.0, 3.0, and 4.0wt%Cu single crystal columnar alloys obtained from PF simulations in this work. The parameters used in Eq. (19) were, $\beta = 0.06$, $\mu = 1 \times 10^{-3}$ Pa s, $\dot{\epsilon}_p = 10^{-4}$ s $^{-1}$. As there is a variability in the spacing λ_1 , the average values calculated from simulated microstructures are used. **There are $\lambda_1 = 3.09, 4.00$, and $4.15 \mu\text{m}$ in Al-2.0, 3.0, and 4.0wt%Cu alloys, respectively.** Fig. 10 presents Kou's HCS parameter ($|dT/d\sqrt{f_s}|$) calculated from the same PF simulations used in

Fig. 9. It is found that the Al-3.0wt%Cu alloy yields the highest HCS index (maximum in the Λ -curve shown in both Figures). For Al-2.0wt%Cu, the existence of short liquid channels ending at relatively high temperatures is the major reason for low HCS. In contrast, a reduced cracking tendency Al-4.0wt%Cu can be expected due to a relatively high liquid fraction at T_e .

Our HCS predictions obtained by combining information from PF simulations with the RGD/Kou models can be compared with available experiments. The results shown here used typical solidification conditions for low speed laser/electron beam welding processes, for which the maximum HCS is predicted to be around 3.0wt% in Al-Cu alloys. These results are consistent with the work of Michaud et al., who also observed the peak of HCS at about 3.5wt%Cu in laser welding of Al-Cu alloys [40]. Other experimental research on hot cracking tendency of Al-Cu alloys in different solidification processes are summarized in Ref. [3]. In general, most experiments find the characteristic Λ -shape curve, as in Figs. 9 and 10. However, the nominal composition yielding the highest HCS have also been observed to be different in some cases. The reason for this is likely that grain structures and microstructures within grains contain non-equilibrium features that can vary from sample to sample, and can yield a significant variation in HCS. These features, in turn, depend on solidification processing conditions. Ideally, a larger ensemble of grain structures would be needed to be simulated to produce a statistically significant measure of HCS for different nominal compositions.

We can infer that coarse columnar grains are more prone to hot cracking compared to finer equiaxed grains. Thus, grain refinement is an efficient mean to avoid hot cracking [38]. However, given the variability in model predictions that can arise due to kinetics and microstructure variability, care needs to be taken to ensure that solidification conditions used to predict the parameters of HCS models adequately capture the macrostructural conditions in experiments. The results of this study suggest that the combination of quantitative PF simulation data with existing hot cracking models can provide a good tool for better predictions of HCS in alloys.

In this work, as we focused on solidification under welding conditions, where microstructures are mainly cellular. Under traditional casting conditions, dendrites are the dominant structure of grains. In terms of effects on HCS, dendrites can be more complicated than cell structure due to side branches. The stochastic feature of sidebranching [43] and the growth and coarsening of secondary arms [44] make coalescence of dendrite structure complex. Moreover, the side branches can nevertheless affect interdendritic flow. This can be seen from the Carman-Kozeny equation in which the permeability of the mushy zone is related to $f_s(T)$ and the characteristic length λ_i by $K = [\lambda_i^2(1 - f_s)^3]/[180f_s^2]$. Normally, the λ_1 is the primary spacing for cell structures and the secondary spacing for dendrites. It is also possible to quantify the interdendritic flow by coupling PF-simulated microstructures with the fluid flow calculations [45].

While the basic mechanisms of hot cracking in 3D are also present in 2D, microstructure connectivity and liquid feeding is more complex in 3D, which can affect HCS. As shown by Tourret et al. [46], there is a difference in the solute diffusion field and final redistribution profiles for 2D versus 3D which can further alter microstructure length. In addition, connectivity of liquid channels can be different in 3D compared to 2D case [47]. It is plausible that the symmetry of the single and bi-crystal grains studied in our work makes it reasonable to compare corresponding 2D and 3D single/bi-crystal systems. This is also consistent with the good comparison of our results to experiments. Due to recent development of computer technology, large-scale 3D phase-field simulations are now viable [46, 48–50]. We are preparing a future 3D work on more complex morphologies using a new 3D parallel, adaptive mesh refinement algorithm to access large scale polycrystalline systems.

5. Conclusions

Segregation and morphology of liquid channels during columnar growth of Al-Cu single crystals and bi-crystals were studied using PF simulations. The results show that the back-diffusion is weak in Al-Cu alloys but it can be important for

other alloys with lower eutectic temperatures. The relative value of the coalescence temperature to the eutectic temperature were examined in the context of liquid channel formation versus liquid drop coalescence in single crystal columnar growth. Liquid channels are shown to coalesce into droplets above T_e for Al-2.0, 3.0wt%Cu alloys, while for Al-4.0wt%Cu alloys liquid at channel roots becomes metastable below T_e and can thus transform to eutectic before coalescence. Simulations of high-angle bi-crystal growth under convergent and divergent growth conditions were examined. It was shown that solute pile up in front of convergent dendritic crystal leads to lateral diffusion away from inter-grain channels, which results in less segregation in the intergranular liquid channels, and ultimately, in grain boundaries. For larger misorientation, a shorter intergranular liquid channel is expected due to lower segregation, which leads to reduced HCS.

This work combined hot cracking models in the literature with information about $f_s(T)$ computed from a quantitative PF model of directional solidification. We demonstrated how this composite numerical modelling combination can be used to predict the nominal composition giving the highest HCS in welding of Al-Cu alloys, with result that were consistent with Al-Cu welding experiments. We propose that combining mean-field type HSC models with input parameters computed from pre-calculated solidification data sets obtained from PF simulations, can provide a practical platform for predicting HCS.

A natural extension of this work is the further development of a phase-field model that combines the quantitative features of models such as the one presented here with the self-consistent nucleation and growth of primary and secondary phases inside liquid channels. This will be the focus of an upcoming study.

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References

- [1] W. Kurz, D. Fisher, Fundamentals of solidification, 4th Edition, Trans Tech Publications Ltd, Switzerland, 1998.
- [2] J. A. Dantzig, M. Rappaz, Solidification, EPFL press, 2009.
- [3] D. Eskin, Suyitno, L. Katgerman, Mechanical properties in the semi-solid state and hot tearing of aluminium alloys, Prog. Mater. Sci. 49 (5) (2004) 629–711.
- [4] M. Rappaz, A. Jacot, W. Boettinger, Last-stage solidification of alloys: theoretical model of dendrite-arm and grain coalescence, Metall. Mater. Trans. A 34 (3) (2003) 467–479.
- [5] J. Luo, V. Gupta, D. Yoon, H. Meyer III, Segregation-induced grain boundary premelting in nickel-doped tungsten, Appl. Phys. Lett. 87 (23) (2005) 231902.
- [6] J. Luo, H. Cheng, K. M. Asl, C. J. Kiely, M. P. Harmer, The role of a bi-layer interfacial phase on liquid metal embrittlement, Science 333 (6050) (2011) 1730–1733.
- [7] W. J. Boettinger, J. A. Warren, C. Beckermann, A. Karma, Phase-field simulation of solidification, Annu. Rev. Mater. Res. 32 (1) (2002) 163.
- [8] L.-Q. Chen, Phase-field models for microstructure evolution, Annu. Rev. Mater. Res. 32 (1) (2002) 113–140.
- [9] A. Badillo, C. Beckermann, Phase-field simulation of the columnar-to-equiaxed transition in alloy solidification, Acta Mater. 54 (8) (2006) 2015–2026.
- [10] H. Xing, X. Dong, C. Chen, J. Wang, L. Du, K. Jin, Phase-field simulation of tilted growth of dendritic arrays during directional solidification, Int. J. Heat Mass Transfer 90 (2015) 911–921.
- [11] B. Böttger, M. Apel, B. Santillana, D. Eskin, Phase-field modelling of microstructure formation during the solidification of continuously cast low carbon and hsla steels, in: IOP Conference Series: Materials Science and Engineering, Vol. 33, IOP Publishing, 2012, p. 012107.
- [12] B. Böttger, G. Schmitz, B. Santillana, Multi-phase-field modeling of solidification in technical steel grades, Trans. Indian Inst. Met. 65 (6) (2012) 613–615.
- [13] B. Böttger, M. Apel, B. Santillana, D. Eskin, Relationship between solidification microstructure and hot cracking susceptibility for continuous casting of low-carbon and high-strength low-alloyed steels: a phase-field study, Metall. Mater. Trans. A 44 (8) (2013) 3765–3777.
- [14] N. Ofori-Opoku, N. Provatas, A quantitative multi-phase field model of polycrystalline alloy solidification, Acta Mater. 58 (6) (2010) 2155–2164.
- [15] B. Echebarria, R. Folch, A. Karma, M. Plapp, Quantitative phase-field model of alloy solidification, Phys. Rev. E 70 (6) (2004) 061604.
- [16] A. Farzadi, M. Do-Quang, S. Serajzadeh, A. Kokabi, G. Amberg, Phase-field simulation of weld solidification microstructure in an Al-Cu alloy, Modell. Simul. Mater. Sci. Eng. 16 (6) (2008) 065005.

- [17] W. Read, W. Shockley, Dislocation models of crystal grain boundaries, *Phys. Rev.* 78 (3) (1950) 275.
- [18] P. R. Cantwell, M. Tang, S. J. Dillon, J. Luo, G. S. Rohrer, M. P. Harmer, Grain boundary complexions, *Acta Mater.* 62 (2014) 1–48.
- [19] B. Echebarria, A. Karma, S. Gurevich, Onset of sidebranching in directional solidification, *Phys. Rev. E* 81 (2) (2010) 021608.
- [20] S.-Z. Lu, J. Hunt, P. Gilgen, W. Kurz, Cellular and dendritic growth in rapidly solidified Al-Fe and Al-Cu alloys, *Acta Metall. Mater.* 42 (5) (1994) 1653–1660.
- [21] N. Provatas, N. Goldenfeld, J. Dantzig, Adaptive mesh refinement computation of solidification microstructures using dynamic data structures, *J. Comput. Phys.* 148 (1) (1999) 265–290.
- [22] N. Provatas, N. Goldenfeld, J. Dantzig, Efficient computation of dendritic microstructures using adaptive mesh refinement, *Phys. Rev. Lett.* 80 (15) (1998) 3308.
- [23] J. Liu, S. Kou, Effect of diffusion on susceptibility to cracking during solidification, *Acta Mater.* 100 (2015) 359–368.
- [24] J. Liu, S. Kou, Crack susceptibility of binary aluminum alloys during solidification, *Acta Mater.* 110 (2016) 84–94.
- [25] S. Kou, *Welding Metallurgy*, 2nd Edition, John Wiley & Sons, Inc., 2003.
- [26] J. Liu, H. P. Duarte, S. Kou, Evidence of back diffusion reducing cracking during solidification, *Acta Mater.* 122 (2017) 47–59.
- [27] Suyitno, V. I. Savran, L. Katgerman, D. G. Eskin, Effects of alloy composition and casting speed on structure formation and hot tearing during direct-chill casting of Al-Cu alloys, *Metall. Mater. Trans. A* 35 (11) (2004) 3551.
- [28] Suyitno, D. Eskin, L. Katgerman, Structure observations related to hot tearing of Al-Cu billets produced by direct-chill casting, *Mater. Sci. Eng. A* 420 (1) (2006) 1–7.
- [29] N. Wang, S. Mokadem, M. Rappaz, W. Kurz, Solidification cracking of superalloy single- and bi-crystals, *Acta Mater.* 52 (11) (2004) 3173–3182.
- [30] B. Cantor, G. Chadwick, The growth crystallography of unidirectionally solidified Al-Al₃Ni and Al-Al₂Cu eutectics, *J. Cryst. Growth* 23 (1) (1974) 12–20.
- [31] Y. Mishin, W. Boettinger, J. Warren, G. McFadden, Thermodynamics of grain boundary premelting in alloys. I. phase-field modeling, *Acta Mater.* 57 (13) (2009) 3771–3785.
- [32] K. Elder, M. Grant, Modeling elastic and plastic deformations in nonequilibrium processing using phase field crystals, *Phys. Rev. E* 70 (5) (2004) 051605.
- [33] K. Elder, M. Katakowski, M. Haataja, M. Grant, Modeling elasticity in crystal growth, *Phys. Rev. Lett.* 88 (24) (2002) 245701.
- [34] N. Provatas, K. Elder, *Phase-field methods in materials science and engineering*, John Wiley & Sons, 2011.
- [35] H. Emmerich, H. Löwen, R. Wittkowski, T. Gruhn, G. I. Tóth, G. Tegze, L. Gránásy, Phase-field-crystal models for condensed matter dynamics on atomic length and diffusive time scales: an overview, *Adv. Phys.* 61 (6) (2012) 665–743.
- [36] N. Provatas, J. Dantzig, B. Athreya, P. Chan, P. Stefanovic, N. Goldenfeld, K. Elder, Using the phase-field crystal method in the multi-scale modeling of microstructure evolution, *JOM* 59 (7) (2007) 83–90.
- [37] S. Kou, A simple index for predicting the susceptibility to solidification cracking, *Weld. J.* 94 (12) (2015) 374S–388S.
- [38] J. Spittle, A. Cushway, Influences of superheat and grain structure on hot-tearing susceptibilities of Al-Cu alloy castings, *Met. Technol.* 10 (1) (1983) 6–13.
- [39] I. Novikov, *Hot-shortness of Nonferrous Metals and Alloys*, Nauka, 1966.
- [40] E. Michaud, H. Kerr, D. Weckman, Temporal pulse shaping and solidification cracking in laser welded Al-Cu alloys, in: H. Smartt, J. Johnson, S. S. A. David (Eds.), *Trends in Welding Research*, ASM International, Materials Park, OH (United States), 1995, p. 154.
- [41] W. Pumphrey, J. Lyons, Cracking during the casting and welding of the more common binary aluminium alloys, *J. Inst. Met.* 74 (9) (1948) 439.
- [42] C. Cross, D. Olson, Hot tearing model to assess aluminum weldability, *Aluminum Alloys—Their Physical and Mechanical Properties* (1986) 1869–1875.
- [43] A. Karma, W.-J. Rappel, Phase-field model of dendritic sidebranching with thermal noise, *Phys. Rev. E* 60 (4) (1999) 3614.
- [44] D. Kammer, P. Voorhees, The morphological evolution of dendritic microstructures during coarsening, *Acta Mater.* 54 (6) (2006) 1549–1558.
- [45] C. Puncreobutr, A. Phillion, J. Fife, P. Lee, Coupling in situ synchrotron x-ray tomographic microscopy and numerical simulation to quantify the influence of intermetallic formation on permeability in aluminium-silicon-copper alloys, *Acta Mater.* 64 (2014) 316–325.
- [46] D. Tourret, Y. Song, A. Clarke, A. Karma, Grain growth competition during thin-sample directional solidification of dendritic microstructures: A phase-field study, *Acta Mater.* 122 (2017) 220–235.
- [47] M. Sistaninia, A. Phillion, J.-M. Drezet, M. Rappaz, Three-dimensional granular model of semi-solid metallic alloys undergoing solidification: Fluid flow and localization of feeding, *Acta Mater.* 60 (9) (2012) 3902–3911.
- [48] T. Takaki, S. Sakane, M. Ohno, Y. Shibuta, T. Shimokawabe, T. Aoki, Large-scale phase-field studies of three-dimensional dendrite competitive growth at the converging grain boundary during directional solidification of a bicrystal binary alloy, *ISIJ Int.* 56 (8) (2016) 1427–1435.
- [49] T. Takaki, S. Sakane, M. Ohno, Y. Shibuta, T. Shimokawabe, T. Aoki, Primary arm array during directional solidification of a single-crystal binary alloy: Large-scale phase-field study, *Acta Mater.* 118 (2016) 230–243.
- [50] Y. Shibuta, M. Ohno, T. Takaki, Solidification in a supercomputer: from crystal nuclei to dendrite assemblages, *JOM* 67 (8) (2015) 1793–1804.
- [51] S. Liu, R. Napolitano, R. Trivedi, Measurement of anisotropy of crystal-melt interfacial energy for a binary Al-Cu alloy, *Acta Mater.* 49 (20) (2001) 4271 – 4276.

Table 1: Physical properties of Al-Cu alloys used in the PF simulations [1, 51]

Melting temperature of Al, T_m	933.47 K
Liquidus slope, m	-2.6 K/wt%
Partition coefficient, k	0.14
Liquid diffusion coefficient, D_l	$3.0 \times 10^{-9} \text{ m}^2\text{s}^{-1}$
Solid diffusion coefficient, D_s	$3.0 \times 10^{-13} \text{ m}^2\text{s}^{-1}$
Anisotropy of surface energy, ϵ_4	0.01
Gibbs-Thompson coefficient, Γ	$2.4 \times 10^{-7} \text{ Km}$

Tables

List of Figures

- 1 Schematic diagram illustrating the effect of nominal composition on liquid channels of alloys with (a) low, (b) moderate, and (c) high concentration. 15
- 2 Grain boundary energy in the phase field model relative to a characteristic solid-liquid interface energy of the model: (a) $\gamma_{gb}^{max}/\gamma_{sl}$ versus driving force coefficient, and (b) γ_{gb}/γ_{sl} versus misorientation angle. 15
- 3 Typical liquid channel morphologies during single crystal columnar growth of Al-Cu alloys with different nominal compositions. The T_m (melting), T_l (liquidus), T_s (solidus), and T_e (eutectic) isotherms are indicated. 16
- 4 Solid fraction f_s vs. temperature T curves calculated from PF simulations and from the Scheil equation for Al-2.0,3.0, and 4.0wt%Cu alloys. 16
- 5 f_s vs. T curves for an Al-3.0wt%Cu alloy calculated from the PF simulations with different solid diffusion coefficients. 16
- 6 Liquid channels in bi-crystal columnar growth of a simulated (a) Al-2.0wt%Cu and (b) Al-4.0wt%Cu alloy. The shadowed areas are enlarged below to show details. T_m , T_l , T_s and T_e have the same meaning as in Figure 3. . . . 17

- 7 Solute distribution within liquid channels in bi-crystal columnar growth of a simulated Al-2.0wt%Cu alloy for three misorientation angles, (a) convergent growth (b) divergent growth. 17
- 8 Average solute composition at grain boundaries versus misorientation for the convergent and divergent columnar bi-crystal growth cases of the Al-2.0wt%Cu alloy data in Figure 7. 18
- 9 Computed solid fraction (f_s^{channel}) and the corresponding calculated pressure drop (ΔP) versus temperature for three nominal alloy compositions. The plots were computed from the single crystal simulation data in Figure 3. The rightmost curves for each alloy correspond to the ΔP , with the maximum of ΔP illustrated for the case of the 4.0wt%Cu alloy. Dotted points connecting maxima of ΔP indicate the Λ -curve. 18
- 10 Computed solid fraction (f_s^{channel}) and the corresponding $|dT/d\sqrt{f_s}|$ versus temperature for three nominal alloy compositions. The plots were computed from the single crystal simulation data in Figure 3. The rightmost curves for each alloy correspond to $|dT/d\sqrt{f_s}|$, with the maximum of $|dT/d\sqrt{f_s}|$ illustrated for the case of the 4.0wt%Cu alloy. Dotted points connecting maxima of $|dT/d\sqrt{f_s}|$ indicate the Λ -curve. 18

Figures

Figure 1: Schematic diagram illustrating the effect of nominal composition on liquid channels of alloys with (a) low, (b) moderate, and (c) high concentration.

Figure 2: Grain boundary energy in the phase field model relative to a characteristic solid-liquid interface energy of the model: (a) $\gamma_{gb}^{max}/\gamma_{sl}$ versus driving force coefficient, and (b) γ_{gb}/γ_{sl} versus misorientation angle.

Figure 3: Typical liquid channel morphologies during single crystal columnar growth of Al-Cu alloys with different nominal compositions. The T_m (melting), T_l (liquidus), T_s (solidus), and T_e (eutectic) isotherms are indicated.

Figure 4: Solid fraction f_s vs. temperature T curves calculated from PF simulations and from the Scheil equation for Al-2.0, 3.0, and 4.0wt%Cu alloys.

Figure 5: f_s vs. T curves for an Al-3.0wt%Cu alloy calculated from the PF simulations with different solid diffusion coefficients.

Figure 6: Liquid channels in bi-crystal columnar growth of a simulated (a) Al-2.0wt%Cu and (b) Al-4.0wt%Cu alloy. The shadowed areas are enlarged below to show details. T_m , T_l , T_s and T_e have the same meaning as in Figure 3.

Figure 7: Solute distribution within liquid channels in bi-crystal columnar growth of a simulated Al-2.0wt%Cu alloy for three misorientation angles, (a) convergent growth (b) divergent growth.

Figure 8: Average solute composition at grain boundaries versus misorientation for the convergent and divergent columnar bi-crystal growth cases of the Al-2.0wt%Cu alloy data in Figure 7.

Figure 9: Computed solid fraction (f_s^{channel}) and the corresponding calculated pressure drop (ΔP) versus temperature for three nominal alloy compositions. The plots were computed from the single crystal simulation data in Figure 3. The rightmost curves for each alloy correspond to the ΔP , with the maximum of ΔP illustrated for the case of the 4.0wt%Cu alloy. Dotted points connecting maxima of ΔP indicate the Λ -curve.

Figure 10: Computed solid fraction (f_s^{channel}) and the corresponding $|dT/d\sqrt{f_s}|$ versus temperature for three nominal alloy compositions. The plots were computed from the single crystal simulation data in Figure 3. The rightmost curves for each alloy correspond to $|dT/d\sqrt{f_s}|$, with the maximum of $|dT/d\sqrt{f_s}|$ illustrated for the case of the 4.0wt%Cu alloy. Dotted points connecting maxima of $|dT/d\sqrt{f_s}|$ indicate the Λ -curve.

***Graphical Abstract**

(a) Al-2.0wt%Cu

(b) Al-3.0wt%Cu

(c) Al-4.0wt%Cu