Multiphase-field modelling of hydrogen pore evolution during alloy solidification

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Abstract. Gas porosity is recognized as one of the most common defects that can severely deteriorate the mechanical properties of solidified materials. Simulating the gas porosity in castings is challenging due to intricate multiphase interaction. In this work, a multiphase-field model is developed to simulate the evolution of both solid phase and hydrogen pore during solidification in the Al-Cu alloy. The driving forces for the solid-liquid and liquid-gas transitions are the undercooling and pressure difference respectively. Results show that the presence of hydrogen pore substantially changes the dendrite network. The Cu element accumulates near the solid-liquid interface due to solute partition. The pore causes a local hydrogen reservoir and Cu vacuum region, which elevates the average hydrogen content and retards the dendrite growth by blocking Cu diffusion.

1. Introduction
Gas porosity in the interdendritic region of castings deteriorates mechanical properties of solidified materials, such as becoming crack source and impairing fatigue strength of engineering parts. The size, distribution, and morphology of the gas porosity change the eventual microstructure morphology by influencing both heat and mass transfer during solidification. Revealing the solid-liquid-gas interaction, together with the transport of solute and gas components, is important but challenging in metallurgy and applied physics [1].

Extensive experimental studies, including in-situ observation [2] and X-ray tomography [3], broaden our insight on the solid-liquid-gas interaction and subsequent porosity morphology. Nevertheless, the real-time precise measurements of the time-dependent quantities such as solute concentration and porosity distribution are still inaccessible for quantitative characterization. On the other hand, large amounts of modelling work are performed to predict the formation of porosity in castings. Lee et al. [4] reviewed the published models in the last century and classified those models into five groups by comparing their benefits, limitations and effectiveness. Those models focus more on the mean-field evaluation of porosity volume fraction and pore size, and they ignore the morphological evolution of solid network and the distribution of both solute and gas components.

As a powerful numerical tool to model microstructure evolution, the phase-field method (PFM) can recover Gibbs-Thomson effect and diffusion effect with rigor physics. An order parameter named the phase-field variable is introduced to characterize different physical states, which is beneficial to handle...
the evolution of complex pattern by avoiding explicit interface tracking. However, there is no mature
PFM to reproduce the complex solid-liquid-gas interaction during solidification to our best knowledge.
Felberbaum and Jacot [5] proposed a preliminary PFM to describe pore shape within static interdendritic
liquid channels, and later their research team [6] further modified this model by using the multiphase-
field concept to satisfy the mechanical and chemical equilibrium conditions at the triple junction.
However, the solid growth is not considered and the dendrite array is artificially predefined. Carré et al. 
[7] developed another PFM to investigate the evolution of hydrogen pore in pure aluminum. This model
is a modified version of the multiphase PFM developed by Eiken et al. [8], and it can handle large
volume change of hydrogen pore. But the solute diffusion which is unavoidable in multicomponent
system is not considered, and the solute redistribution caused by the presence of gas porosity remains
unknown.

In this work, we develop a new multiphase-field model to investigate the complex solid-liquid-gas
interaction. This model accounts for the growth of solid phase and the distribution of both solute and
gas components, which allows for a direct description of micro pores in a more realistic dendrite solid
network. The hydrogen pore is modeled as a typical case of the gas porosity. The objective of the present
work is to present the multiphase-field approach for a numerical description of the combined evolution
of solid phase, hydrogen pore, solute concentration and gas content during alloy solidification.

2. Mathematical model

2.1. Multiphase-field model

A solid-liquid-gas multiphase-field model is developed to numerically describe the evolution of both
solid phase and hydrogen pore during alloy solidification. The problem of interest represents a small
section of a dendrite network. Three order parameters named the phase-field variables, $\phi_i$, $\phi_s$, and $\phi_h$, are introduced to denote different phases, which correspond to local volume fractions and maintain at 1 at
any location. $\phi_i$ changes from 0 to 1 smoothly over an assumed diffuse interface and becomes
1 in the bulk $i$ phase. Based on thermodynamic consistency, the evolution equations of $\phi_i$ are derived as

$$
\tau_i \frac{\partial \phi_i}{\partial t} = K_i \left( \frac{\sigma_i}{h_i} \nabla^2 \phi_i - 2\phi_i (1-\phi_i)(1-2\phi_i) - \Theta_i + 15\phi_i^2 \phi_j^2 \frac{\Delta G_{i\ell}}{h_{i\ell}} - \frac{1}{3} \Lambda \right)
$$

(1)

$$
\tau_i \frac{\partial \phi_s}{\partial t} = K_i \left( \frac{\sigma_i}{h_i} \nabla^2 \phi_s - 2\phi_s (1-\phi_s)(1-2\phi_s) - \Theta_s - 15\phi_s \phi_j^2 \frac{\Delta G_{s\ell}}{h_{s\ell}} - 15\phi_s^2 \phi_j^2 \frac{\Delta G_{s\ell}}{h_{s\ell}} - \frac{1}{3} \Lambda \right)
$$

(2)

$$
\tau_s \frac{\partial \phi_h}{\partial t} = K_s \left( \frac{\sigma_s}{h_s} \nabla^2 \phi_h - 2\phi_h (1-\phi_h)(1-2\phi_h) - \Theta_h + 15\phi_h \phi_j^2 \frac{\Delta G_{h\ell}}{h_{h\ell}} - \frac{1}{3} \Lambda \right)
$$

(3)

with

$$
\Lambda = \sum_i \left[ \frac{\sigma_i}{h_i} \nabla^2 \phi_i - 2\phi_i (1-\phi_i)(1-2\phi_i) - \Theta_i \right]
$$

(4)

$$
\Theta_i = \frac{\partial}{\partial \phi_i} \left[ a_i \phi_i^2 \phi_j^2 (2\phi_i \phi_j + 3\phi_i) \right] + \frac{\partial}{\partial \phi_j} \left[ b_j \phi_j^2 \phi_k^2 \phi_i \right]
$$

(5)

where the introduction of $\Lambda$ is to satisfy the constraint $\sum \phi_i = 1$, $\Theta_i$ corresponds to the triple-well potential
with a tunable height of the saddle point on each binary interface [9], and $a_i$ and $b_j$ are two constants. $\tau_i$
$K_i$, $\sigma_i$, and $h_i$ are the relaxation time, interface mobility, interface energy, and potential energy coefficient
which are dependent on the phase interfaces, respectively. It is assumed that $\tau_i = \tau_e = \tau_0$, $h_i = h_l = h_e$,
where $\tau_0$ is the time scaling. $K_i$ can be used to adjust the phase-change rate, and a larger $K_i$ corresponds
to a faster interface advancing velocity. $\Delta G_{i\ell}/h = p_i - p_l$ is the driving force for the liquid-gas phase
change, where $p_i$ is the pressure in the $i$ phase. $\Delta G_{i\ell}/h$ is the driving force for the solid-liquid phase
change and is expressed as \(-8\dot{\theta} (\theta + MC_x U) / 15\) by mapping the multiphase-field equations to the solid-liquid phase-field model developed by Karma et al. [10, 11], where \(\lambda, \theta, M, C_\infty, \text{and } U\) are the coupling constant, dimensionless undercooling, dimensionless liquidus slope, far-field solute concentration, and dimensionless solute concentration, respectively, all of which have the same definitions as those in [11].

It is noted that the driving force for the solid-gas phase change is zero from equations (1)-(3), i.e. the interaction between the solid and gas phases is ignored. The gas phase only interacts with the liquid phase but liquid interacts with both solid and gas.

The evolution of the solute concentration and hydrogen content is governed by

\[
\frac{\partial C^X}{\partial t} = \nabla \cdot (D^X \nabla C^X) + R(X)
\]  

(6)

where \(X\) denotes Cu for the Al-Cu alloy and hydrogen (H) for the gas pore, and \(D^X\) is the diffusivity of \(X\) and is determined by the volumetric averaging approach, i.e., \(D^X = \phi_s D_s^X + \phi_l D_l^X + \phi_g D_g^X\). \(R(X)\) denotes the partition of \(X\) at the phase interfaces, i.e.,

\[
R(Cu) = n_s n_l C^{Cu} (1 - k^{Cu}) \frac{d\phi_s}{dt}
\]

(7)

\[
R(H) = n_s n_l C^{H} (1 - k^{H}) \frac{d\phi_s}{dt}
\]

(8)

where \(n_i (i = s, l, g)\) is a step function, i.e., \(n_i = 1\) if \(\phi_i > 0\) and \(n_i = 0\) otherwise. \(k^{Cu}\) and \(k^{H}\) are the equilibrium partition coefficients of Cu and H at the solid-liquid interface, respectively.

The region inside the pore is considered to be a local vacuum region of Cu element, i.e., Cu concentration inside the pore is zero [12]. The hydrogen content inside the pore is assumed uniform and is connected with the pressure by the perfect gas law. By combining the perfect gas law and the Sievert law, the gas content at \(\phi_g > 0\) is obtained as

\[
C^H = \frac{2p_g}{RT} \phi_g + k^H S_s \left[ \left( \frac{P_g}{P_0} \right)^{\frac{1}{\phi_s}} + S_s \left( \frac{P_g}{P_0} \right)^{\frac{1}{\phi_g}} \right]
\]

(9)

where the unit of \(C^H\) is atomic moles m\(^{-3}\), \(R, T, P_0\) and \(S_s\) are the universal gas constant, melt temperature, atmospheric pressure, and Sievert constant for the liquid with the unit atomic moles m\(^{-3}\).

2.2. Mapping to the two-phase solidification

By setting \(\phi_i (i = s, l, g) = 0\), the multiphase-field equation is restored to the governing equation of the two-phase system. Here, taking \(\phi_g = 0\) for instance, introduce \(p = 1 - 2\phi_i\) and rewrite equations (1)-(2) in a unified form:

\[
\tau_0 \frac{\partial p}{\partial t} = K_d \left( \frac{\sigma_{sl}}{h_{sl}} \nabla^2 p + p - p^\gamma - \left( 1 - p^\gamma \right)^2 \lambda (\theta + MC_x U) \right)
\]

(10)

where \(K_d = 1, \sigma_{sl}/h_{sl} = W^2\), and \(W\) is the interface thickness. The time and length are rescaled by \(t^* = t/t_0\) and \(x^* = x/W\). Equation (10) is the same as the thermostolutal phase-field equation of the binary alloy proposed by Ramirez et al. [11], and it is restored to the phase-field equation of a pure melt developed by Karma et al. [10], if the solute concentration \(U\) is neglected. Based on the definition of the antitraping current [11] and the dimensionless expressions of \(\theta\) and \(U\),

\[
\frac{\theta}{T - T_M - mC_\infty} = \frac{2C/C_\infty}{\Delta T_0} \frac{1 + k - (1 - k)p}{1-k} - 1
\]

(11)

the solute field equation (6) combining with equation (7) is restored to
Accordingly, the multiphase-field model is restored to the two-phase solidification phase-field model. After mapping operation, the modeling parameters can be further determined by an asymptotic analysis of the thin-interface limit [11].

3. Results and discussion

Without considering the nucleation process, both the solid seed and a pre-existing hydrogen pore are initialized in the domain. The thermo-physical parameters are according to the Al - 4 wt% Cu alloy [13], and the other modeling parameters are listed in Table 1. It is noted that the common symbol of hydrogen content in the casting industry is [H] and the corresponding unit is cc/100g. A unit conversion, $C_H = \rho_L [H]/2241$, needs to be performed, where $\rho_L$ is the alloy liquid density [14]. Since the computational domain is a small window centered on one pore and is much smaller than the space related to one pore, the initial hydrogen content needs to be large enough to offset that [6]. Once the initial pore radius $r_g$ is given, the pressure inside the pore is determined by the Laplace pressure condition:

$$p_g = p_l + \gamma_{lg}/r_g$$  

(13)

where $\gamma_{lg}$ is the liquid-gas interface energy.

The temperature is assumed isothermal, and zero-Neumann boundary conditions are set at all sides for all variables including the three phase-field variables, Cu concentration, hydrogen content, temperature, and pressure.

### Table 1. Parameters used in the phase-field simulations [6].

| Parameter                              | Value   |
|----------------------------------------|---------|
| $C_H^\alpha$, far-field hydrogen content in liquid, cc/100g | 1.0     |
| $D_H$, diffusivity in liquid, m$^2$/s   | $1 \times 10^{-6}$ |
| $S_l$, Sievert constant in liquid, mol/m$^3$ | 0.69     |
| $p_l$, pressure in liquid, atm          | 0.9     |
| $p_0$, atmosphere pressure, atm        | 1.0     |
| $\gamma_{sl}$, solid-liquid interface energy, J/m$^2$ | 0.15     |
| $\gamma_{lg}$, liquid-gas interface energy, J/m$^2$ | 0.868   |
| $\rho_L$, alloy liquid density, kg/m$^3$ | $2.61 \times 10^3$ |
| $\theta$, dimensionless undercooling   | -0.25   |
| $R$, universal gas constant, J/(mol K)  | 8.314   |

3.1. Interaction between single dendrite and hydrogen pore

The seed with radius of 1.6 is initialized at the domain center, and the pore with radius of 16 is set at (0.5X, 0.2Y), where X = Y = 512 is the domain size in the unit of W. Figure 1 shows the evolution of both solid phase and hydrogen pore during solidification. The two rows correspond to the cloud map of the phase-field contour and Cu concentration. At the early stage, both the solid phase and the hydrogen pore evolve freely without interaction. The face-centered-cubic Al-Cu dendrite exhibits four-fold symmetry and the pore maintains the circle shape. Because of the solute partition, the Cu element
accumulates at the solid-liquid interface, especially at the dendrite root. The pore expands by absorbing the hydrogen dissolved in liquid until reaching the pressure equilibrium. When the downward dendrite tip approaches the pore, the dendrite wraps the pore by growing along the pore boundary. The pore expands by pressing the liquid aside, which causes local enrichment of Cu element around the pore and decrease of the dendrite growth velocity.

![Figure 1](image1.png)

**Figure 1.** Evolution of the dendrite growth in the presence of hydrogen pore. Each row corresponds to the cloud map of the phase-field contour and Cu concentration, respectively.

Figure 2 shows the change of the three phase-field variables along the direction designated by line I in figure 1(c). The phase-field variables change smoothly at the phase interfaces, and the sum maintains at one at any location. Taking the liquid-gas interface in figure 2(b) for instance, $\phi_l = \phi_g = 0.5$ and $\phi_s = 0$ at $x/X = 0.142$. Due to the diffuse nature in the phase-field model, a triple junction is observed at $x/X = 0.252$, where $\phi_l = \phi_g = 0.38$ and $\phi_s = 0.24$. The solid-liquid-gas triple junction is like the triple point during eutectic solidification.

![Figure 2](image2.png)

**Figure 2.** Three phase-field variables versus the distance along the direction designated by line I in figure 1(c). (b), (c) and (d) are the local enlarged images of (a).

The pore is a local Cu vacuum region which acts like an obstacle blocking Cu diffusion. When the diffusion of the rejected Cu element from the solidified dendrite is hindered, a local Cu enrichment region forms between the downward dendrite tip and pore boundary. According to the phase diagram, the enriched solute lowers the undercooling and thus slows down the downward solid growth. Such asymmetric growth behaviour is analogous to that under convection [15].
Figure 3 shows the distribution of Cu and H along the directions designated by lines II and III in figure 1(f). Along line II, the distribution is symmetric about the domain centre, and the concentration of both Cu and H obtains the extreme at the solid-liquid interface. After reaching the equilibrium at the solid-liquid interface, the Cu concentration inside the solid phase keeps unchanged. Along line III, the H concentration increases with the distance away from the pore, while that of Cu decreases. The H concentration near the pore boundary is lower than the average value in the liquid. The presence of hydrogen pore causes a local hydrogen reservoir. Thus the H diffuses towards the liquid-gas interface and into the pore, which increases the gas content inside the pore and promotes the pore expansion. The liquid-gas phase change, i.e., pore expansion or movement of the liquid-gas interface, is driven by the pressure difference, which is similar to the work performed by Meidani and Jacot [6].

The pore expands by pressing the liquid aside, and the Cu element accumulates around the pore. As the distance from the pore increases, the Cu concentration decreases until approaching the far-field value. It is noted that the liquid flow induced by the expansion of the pore and resultant convection transport are ignored, which deviates from the practical scenario and makes the concentration around the pore larger than the real value.

3.2. Interaction between multidendrites and hydrogen pore

Ten solid seeds with radius of 1.6 are initialized randomly in the domain, and one pore with radius of 16 is set at (0.5X, 0.2Y), where X = Y = 1024 is the domain size in the unit of W, as shown in figure 4(a). The parameter configuration is the same as that in section 3.1. The multidendrites exhibit four-fold symmetry and grow competitively by impinging on neighbouring dendrite arms. The presence of the pore changes the complex dendritic morphology by inhibiting the solid growth.

Figure 4 shows the comparison of Cu concentration without and with the hydrogen pore. A local high-concentration Cu region exhibits near the pore boundary, but in other location, the distribution of Cu is not disturbed. The enriched Cu has two sources, i.e. solute partition at the solid-liquid interface and solute pileup due to pressed liquid by pore expansion. The distribution of hydrogen is more uniform.
than that of Cu, because the hydrogen diffusivity is about 300 times larger than the Cu diffusivity. The high-concentration H region is retained in the upper-right part due to larger interface area. The pore absorbs the neighbouring hydrogen, which promotes the rejection of hydrogen from the solidified dendrites and thus elevates the average hydrogen content inside the domain, i.e., from 1.77 to 1.95 mol/m³.

The pore usually nucleates at high solid fraction and high hydrogen content. As the temperature decreases, the pore exhibits complex geometrical shape due to numerous contacts with neighbouring solid. The enriched Cu element slows down the solid growth, and the remaining liquid surrounding the pore makes the pore undergo negligible shape change.

The redistributed Cu element changes the relative density of melt, which can cause liquid convection and pore movement. The liquid convection is not considered in the present work and thus the pore centre stays still. In some in-situ observations reported on the directional solidification of organic alloys [2, 16], the bubble is stuck between the two glass covers, and the solid phase can engulf or entrap the pore as the solid-liquid interface advances. Those phenomena occur at a decreasing temperature, and the dendrites can have enough driving force to compensate the effect of the solute enrichment.

![Figure 5. Comparison of Cu concentration without (a) and with (b) the hydrogen pore.](image)

4. Conclusion and remark
A multiphase-field model is developed to simulate dendrite growth in the presence of the hydrogen pore during solidification. The present model incorporates the growth of solid phase, the expansion of hydrogen pore, and the redistribution of both solute and hydrogen at the phase interfaces. This model can be accurately mapped to the two-phase models, and the driving forces for the solid-liquid and liquid-gas phase changes are the undercooling and pressure difference. The presence of hydrogen pore substantially changes the dendrite symmetry by blocking solute diffusion and inhibiting solid growth. The pore acts like a local Cu vacuum region, which causes solute enrichment around the pore, but as a hydrogen reservoir, it elevates the average content of hydrogen by absorbing the neighboring hydrogen and promoting the rejection of hydrogen from the solidified dendrites. The solute-rich liquid surrounding the pore lowers the local undercooling and solidifies later, making the pore grow circularly and undergo less change.

The hydrogen diffusion is considered to be one of the most important factors governing the growth dynamics of the pore. To precisely characterize such growth dynamics, the liquid convection induced by the expansion of the pore and hence the hydrogen transport by convection need to be exploited quantitatively. Besides, the large pore deformation under convection poses a challenge on the conservative characteristic of the model in characterizing the complex topology interface. More sophisticated numerical models which can incorporate all these physical phenomena will be considered in future development.
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