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On the solute coupling at the moving solid/liquid interface during equiaxed solidification

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Integral mass conservation was widely accepted for the solute coupling to solve solute redistribution during equiaxed solidification so far. The present study revealed that the integral form was invalid for moving boundary problems as it could not represent the mass balance at the moving interface. Accordingly, differential mass conservation at the solid/liquid interface was used to solve solute diffusion for spherical geometry. The model was applied for hydrogen diffusion in solidification to validate that the hydrogen enrichment was significant and depended on the growth rate. © 2006 American Institute of Physics. [DOI: 10.1063/1.2336079]

Almost all metallic materials formed through solidification which controls their final microstructures and properties. Technologically speaking, this process has been used for several thousand years. However, it only became a science when Tiller *et al.*¹ introduced the concept of “the constitutional supercooling (CS).” The CS, determined by the solute diffusion (redistribution), has been considered as the foundation of modern solidification theory. In general, there are two key aspects in the solidification, namely, nucleation and crystal growth. Both aspects are mainly controlled by the CS. Therefore, the solute diffusion has been extensively studied both theoretically and experimentally.^{1–10} Many solute diffusion models were developed and some of them are widely accepted as the fundamentals to establish the solidification theory, such as for dealing with the interface instability and the microstructure selection.⁴ Currently, the time-dependent solute redistribution profile, C , can be determined by solving Fick’s second law⁴

$$\frac{1}{D_i} \frac{\partial C_i}{\partial t} = \frac{\partial^2 C_i}{\partial r^2} + \frac{n}{r} \frac{\partial C_i}{\partial r}, \quad (1)$$

with its solute coupling equation^{3,5}

$$\int_{V_L} C_L dr + \int_{V_S} C_S dr = V_d C_0, \quad (2)$$

where i ($=S, L$) represents the parameter in the solid and liquid, respectively; D is the solute diffusion coefficient; r is the coordinate; t is the time; C_0 is the initial concentration of the alloy; V_L , V_S , and V_d are the volume of the liquid, solid, and the entire system, respectively; and $n=0, 1, 2$ represents the diffusion equation for a plate, cylindrical, or a spherical geometry, respectively. Based on these two equations and the boundary conditions, models for solute redistribution for equiaxed solidification^{3,5} and the microsegregation for dendritic growth^{2,4} have been developed. It is of interest to note that the solute and coupling equations do not account for moving boundary problems, although in the real solidification process, the solid/liquid interface moves. For this reason, the validity of the coupled equations is in doubt as it

may cause the following errors for describing solute redistributions.

- (1) Physically, the solute redistribution during solidification is due to the different solubility in the solid and liquid. When the liquid transfers to the solid, extra solute (for the alloy with $k < 1$, where k is solute partition coefficient) will be rejected from the solid and enriched at the solid/liquid interface. The amount of the rejected solute is dependent on the velocity of liquid-to-solid transformation, e.g., the interface velocity. The mass conservation at the interface can be expressed using the following equation:⁴

$$VC_L^*(1-k) = -D_L \left. \frac{\partial C_L^*}{\partial r} \right|_{r=R^*} + D_S \left. \frac{\partial C_S^*}{\partial r} \right|_{r=R^*}, \quad (3)$$

where R^* is the radius of solid during solidification. During the solidification, Eq. (3) must be satisfied. However, the current form of Eq. (2) cannot guarantee this.

- (2) During the unidirectional solidification, moving interfaces are considered in all existing solute models. As a consequence, Eq. (1) can be rewritten as^{1,11}

$$\frac{1}{D_L} \frac{\partial C_L}{\partial t} = \frac{\partial^2 C_L}{\partial x^2} + \frac{V}{D_L} \frac{\partial C_L}{\partial x}, \quad (4)$$

where V is the velocity of the moving interface. Using a first approximation of quasi-steady-state assumption, Tiller *et al.*¹ solved Eq. (4) for solute redistribution in the liquid during directional solidification, which is

$$C_L^* = \frac{C_0}{k} \left[1 - (1-k) \exp\left(-\frac{kV^2}{D_L} t\right) \right], \quad (5)$$

where the asterisk ($*$) states the parameter at the interface. More accurate solution of Eq. (4) has been carried out^{4,6,7,9,10} analytically and/or numerically for different directional solidification processes. All these models indicate that the solute redistribution is directly related to the interface velocity, which plays the most important role in the solute redistribution during solidification.

Since the physical nature of the solute diffusion is exactly the same between directional and equiaxed so-

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lification, it is necessary to consider the effect of the moving interface on solute diffusion for the case of equiaxed solidification. From Eq. (5), it is clearly seen that the interface velocity has a strong influence on the solute redistribution. It is reasonable to believe that the interface velocity must play a similar role in solute redistribution for equiaxed solidification. However, the previous diffusion models²⁻⁵ [refer to Eq. (1)] for equiaxed solidification show that the solute redistribution is directly related to the fraction of solid, f , but *independent* on the interface velocity.

As $f \propto (Vt)^3$, the solute redistribution is actually related to the interface velocity, V . However, the extent of the solute redistribution is the same in a certain alloy if the f is fixed with whatever V by different solidification times. This means that the solute profile against f will be the same with different V , so it was called “independent” on the V . Accordingly, the correct description of diffusion equation in equiaxed solidification should have a similar form for directional solidification, which gives

$$\frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left(\xi^2 \frac{\partial C_i}{\partial \xi} \right) + \frac{VR_f}{D_i} \frac{\partial C_i}{\partial \xi} = 0 \quad \text{with } \xi = (r - Vt)/R_f, \quad (6)$$

where R_f is the radius of the final grain and V assumes as a constant.

- (3) The previous diffusion models can be simplified to the Lever rule^{4,5} when D_i is sufficiently large,⁵ e.g., $D_i \rightarrow \infty$. To demonstrate the problem, we apply these models to hydrogen partitioning and diffusion in aluminum alloy. As an example, the Nastac and Stefanescu model⁵ can be simplified to Lever rule for hydrogen diffusion as the hydrogen diffusion coefficient is very high,¹² e.g., $D_S^H = 4.0 \times 10^{-8} \text{ m}^2/\text{s}$ and $D_L^H = 3.8 \times 10^{-6} \text{ m}^2/\text{s}$. The predicted hydrogen enrichment ahead of the solid/liquid interface by these models²⁻⁵ can be ignored. In contrast, Han and Viswanathan⁸ developed a numerical model and predicted significant hydrogen enrichment during directional solidification of aluminum alloys. They claimed that the hydrogen diffusion in aluminum cannot be described by the Lever rule as porosity nucleation resulted from hydrogen enrichment was observed experimentally. Furthermore, their model predicted that the enrichment of hydrogen at the eutectic front is strongly affected by the solid growth velocity, with the higher the growth rates, the higher the hydrogen enrichment. This means that the previous models for equiaxed solidification are invalid at least for the case of quick solute diffusion.

- With velocity-dependent mass balance condition of Eq. (3), the concentration at the interface can be determined by solving Eq. (6), which gives¹³

$$C_i^* = C_0 \left[1 - \frac{V(1-k)}{D} \right]^{-1}, \quad (7)$$

where $D = -D_L I_L + k D_S I_S$ and

$$I_L = \frac{1}{R} \frac{V}{D_L} \frac{\exp[V(R_f - R^*)/D_L]}{\exp[V(R_f - R^*)/D_L] - (1 + VR_f/D_L)}$$

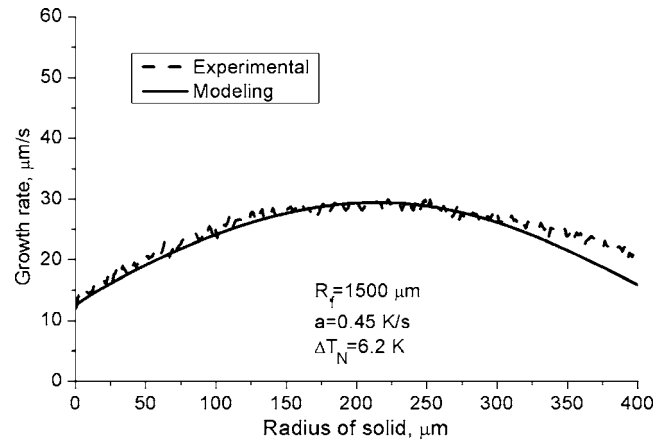


FIG. 1. Relationship between growth rate and radius of solid during equiaxed solidification with $R_f = 1500 \mu\text{m}$, the cooling rate $a = 0.45 \text{ K/s}$, and the nucleation undercooling of the Al–Si eutectic $\Delta T_N = 6.2 \text{ K}$.

$$I_S = -\frac{1}{R^*} + \frac{V}{D_S} \frac{\exp(-VR^*/D_S)}{1 - \exp(-VR^*/D_S)}$$

From Eq. (7), it is clearly seen that the velocity plays an important role on solute redistribution.

To demonstrate the correctness of this model, we applied this model to hydrogen diffusion in an aluminum alloy with very large diffusion coefficients¹⁴ and gained support evidence by an experiment of the porosity formation by hydrogen during the eutectic solidification.¹⁴ In this case, strontium-modified Al–10 wt % Si alloy, e.g., $R_f = 1500 \mu\text{m}$, the cooling rate $a = 0.45 \text{ K/s}$, and the nucleation undercooling of the Al–Si eutectic $\Delta T_N = 6.2 \text{ K}$, was investigated. The velocity-undercooling ($V \sim \Delta T$) relationship was given by $V(\mu\text{m/s}) = 0.33 \Delta T^2$. The hydrogen solution in the bulk melt is $0.05 \text{ mm}/100 \text{ g}$ and k equals to 0.069 from Al–H phase diagram.¹³ Figure 1 shows that the calculated growth rate predicted by a thermal model developed in Ref. 15 agrees very well with the experimental measurement by McDonald *et al.*¹⁴ Under these solidification conditions, the interface concentration of liquid was determined and shown as a solid plot in Fig. 2. In contrast, the concentration plot predicted by previous models shows a flat curve (the dash curve). Comparison of the two results shows that the enrichment of hydrogen at the interface is much higher with the presented model. It is found that the models that include the effect of

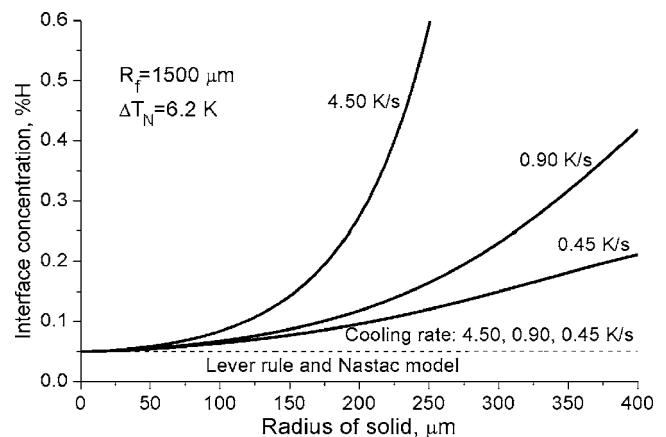


FIG. 2. Relationship between hydrogen concentration at the interface and the radius of solid with different cooling rates.

the moving interface and the solute balance at the solid/liquid interface predicted the hydrogen a significant enrichment. On the contrary, those models that used overall mass conservation coupling to calculate the hydrogen enrichment gave a very small hydrogen enrichment. Since the porosity resulted from hydrogen enrichment was observed,¹⁴ the presented model seems to be a likely model to describe the phenomenon. Figure 2 also shows two plots with higher cooling rate and the results show that the higher the cooling rates, the larger the extent of hydrogen enrichment. This trend is similar to the numerical model developed by Han and Viswanathan.⁸

In conclusion, the previous models for equiaxed solidification and/or for dendritic solute segregation are invalid as they failed to account for the effect of moving interface on solute redistribution. The proposed model developed in this letter is refined to correctly describe the solute redistribution that has been tested in an extreme condition of very fast diffusion of hydrogen in an aluminum alloy. It is obtained that the present model predicted a significant hydrogen enrichment and the hydrogen enrichment was strongly influenced by the cooling rate, which agreed well with the reality of porosity formation during solidification.

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