

Solute trapping model based on solute drag treatment

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Abstract: A solute trapping model is developed based on a so-called solute drag treatment. By adopting a basic approach of phase-field models, and defining the free energy density in the interfacial region, a suitable interface shape function is introduced to derive the current model, in which the equilibrium and non-equilibrium interface behaviours can be described using a dimensionless parameter L (i.e. an important parameter in the present interface shape function). When applying the current model to Si-9%As (molar fraction) alloy with $L=0.5$, a good prediction of the steeper profile for high interface velocity, which is analogous to that using a phase-field model of DANILOV and NESLTER, has been obtained.

Key words: solute trapping; solute drag; diffusive interface

1 Introduction

Solute trapping has been extensively studied since a phenomenon that the solid cadmium concentration in zinc-cadmium alloys could extend the equilibrium solid solubility limit after splat quenching was observed[1]. It is defined as “solute trapping” because the solute atoms seem to be caught by the growing phase although there is a driving force for them to escape from[2], and this phenomenon is broadly studied in pulsed laser annealing experiments[3–6]. So far, solute trapping has been theoretically treated using sharp interface methods[7–12], phase-field methods[13–16] and solute drag methods[17–18].

For sharp interface models, a discontinuity of solute concentration occurs at the interface. Whereas, the phase-field models consider, in a more realistic way, a diffusive interface with a finite thickness and describe dynamic phenomena in both the bulk phases and the interface region in terms of a single formalism. The interface properties change as a function of the phase-field variable ϕ ($\phi=1$ for one phase and $\phi=0$ for the other one) and the variation of ϕ with distance through the interface is determined by a step-wise, local minimization of Gibbs energy in a finite-element procedure[2]. The concentration profile becomes a

continuous function of the coordinate. The specific jump in the concentration at the interface which is typical for a sharp interface formulation disappears and is replaced by a continuous profile with a characteristic maximum near the transition region[16]. As for the solute drag models, a finite thickness of the interface is also assumed, which is similar to the phase-field models. However, it is supposed that the diffusivities and thermodynamic properties change only as functions of distance through the interface.

Compared with the sharp interface models without considering interfacial solute diffusion and the complicated phase-field models, the solute drag treatment gives a relatively simple expression incorporating interfacial solute diffusion. However, the solute drag treatment is generally based on the wedge-shaped[17–18], truncated wedge[19–21] or smooth interface[22]. The above so-called continuous interface models are not really continuous[2]. The solute concentration profile across the interface to the bulk phases changes only continuously but not smoothly, i.e. the diffusive function cannot be described by a uniform formalism.

In the present work, a suitable interface shape function is introduced using a basic approach with of phase-field models, that the free energy density of the interfacial region incorporated with the solute drag

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treatment. On this basis, a relatively simple solute trapping model, with characteristics analogous to phase-field approaches, is obtained.

2 Model derivation

2.1 Interface solute diffusion and solute trapping

For a binary system, i.e. solvent A and solute B, a layer of thickness, δ , exists between liquid and solid phases, where the thermodynamic quantities, such as the solute chemical potential, μ_B , change continuously from solid to liquid. Supposing an ideal solution, μ_B in the interfacial region can be given as

$$\mu_B = \mu_B^0(X) + RT_1 \ln C(X) \quad (1)$$

where μ_B^0 is the standard chemical potential of the solute, R the gas constant, T_1 the interface temperature and C the solute concentration which depends on the coordinate X normal to the moving interface.

Then, the diffusive flux of the solute, J , can be given as

$$-J = \frac{CD_1(X)}{V_m RT_1} \frac{\partial \mu_B}{\partial X} = \frac{D_1(X)}{V_m} \frac{\partial C}{\partial X} + \frac{D_1(X)C}{RT_1 V_m} \frac{\partial \mu_B^0(X)}{\partial X} \quad (2)$$

where V_m is the molar volume, and D_1 the solute diffusion coefficient which also changes continuously from solid to liquid across the interface.

Given a constant V , the composition profile in the interface is expected to reach a steady state. Supposing that the solid-state solute diffusion is always omitted, the mass conservation law gives

$$J = \frac{V(C - C_s)}{V_m} \quad (3)$$

where C_s is the solid concentration adjacent to the interface, and is expected to be C_0 under steady state. From Eqs.(2) and (3), solute diffusion in the interface can be described as

$$\frac{\partial C}{\partial X} + \left(\frac{1}{RT_1} \frac{\partial \mu_B^0(X)}{\partial X} + \frac{V}{D_1} \right) C = \frac{V}{D_1} C_s \quad (4)$$

The solution of Eq.(4) can be expressed as

$$C(X) = \exp \left\{ - \int_0^X \left(\frac{1}{RT_1} \frac{\partial \mu_B^0}{\partial X} + \frac{V}{D_1(X)} \right) dX \right\} \cdot \left\{ \int_0^X \exp \left[\int_0^X \left(\frac{1}{RT_1} \frac{\partial \mu_B^0}{\partial X} + \frac{V}{D_1(X)} \right) dX \right] \frac{C_s V dX}{D_1(X)} + C_s \right\} \quad (5)$$

As compared with CAHN's model [18], Eq.(5) presents no singularity for $V=0$, since the solute diffusion in the solid is not considered here. Following the normal

procedure of the solute drag treatment[17], the non-equilibrium partition coefficient, k , can be deduced as

$$k = \frac{C(0)}{C(\delta)} = \frac{C_s}{C_L} = \exp \left\{ \int_0^\delta \left(\frac{1}{RT_1} \frac{\partial \mu_B^0}{\partial X} + \frac{V}{D_1(X)} \right) dX \right\} \cdot \left\{ \int_0^\delta \exp \left[\int_0^X \left(\frac{1}{RT_1} \frac{\partial \mu_B^0}{\partial X} + \frac{V}{D_1(X)} \right) dX \right] \frac{V dX}{D_1(X)} + 1 \right\}^{-1} \quad (6)$$

In terms of $\eta=X/\delta$, then Eqs. (5) and (6) reduce to

$$C(\eta) = \exp \left\{ - \int_0^\eta \left(\frac{1}{RT_1} \frac{\partial \mu_B^0}{\partial \eta} + \frac{V\delta}{D_1(\eta)} \right) d\eta \right\} \cdot \left\{ \int_0^\eta \exp \left[\int_0^\eta \left(\frac{1}{RT_1} \frac{\partial \mu_B^0}{\partial \eta} + \frac{V\delta}{D_1(\eta)} \right) d\eta \right] \cdot \frac{C_s V \delta d\eta}{D_1(\eta)} + C_s \right\}^{-1} \quad (7)$$

and

$$k = \exp \left\{ \int_0^1 \left(\frac{1}{RT_1} \frac{\partial \mu_B^0}{\partial \eta} + \frac{V\delta}{D_1(\eta)} \right) d\eta \right\} \cdot \left\{ \int_0^1 \exp \left[\int_0^\eta \left(\frac{1}{RT_1} \frac{\partial \mu_B^0}{\partial \eta} + \frac{V\delta}{D_1(\eta)} \right) d\eta \right] \frac{V\delta d\eta}{D_1(\eta)} + 1 \right\}^{-1} \quad (8)$$

Eq.(8) is the general expression for solute trapping in a dilute alloy, obtained from the solute drag treatment. It is clearly shown in Eq.(8) that solute trapping is only influenced by interface diffusion if V is already known. If $V=0$, an equilibrium interface holds, then interface diffusion is solely determined by the gradient of the standard chemical potential $\partial \mu_B^0 / \partial \eta$, and the non-equilibrium partition coefficient reduces to the equilibrium one, k_e . If $V \rightarrow \infty$, then interface diffusion is solely determined by V/D_1 in Eq.(7) or (8), and a complete solute trapping occurs. This coincides with the limiting condition proposed by BAKER for the solute trapping model.

2.2 Interface shape function

In the solute drag treatment, the interface shape function, i.e. the diffusivities and thermodynamic properties as functions of the distance (i.e. η in Eqs.(7) and (8)) through the interface, are given as a priority. In order to obtain the interface solute concentration, $C(\eta)$, and the non-equilibrium partition coefficient k for a given V , $\partial \mu_B^0 / \partial \eta$, and $D_1(\eta)$ in Eqs.(7) and (8) should be known. Generally, different interface shape functions lead to different solute trapping models. Given a

wedge-shaped interface function for $\partial\mu_B^0(\eta)/\partial\eta$, $D_I(\eta)$ can be assumed, respectively, as the solid-state diffusion coefficient, D_S , for half of the interface adjacent to the solid, and as the liquid-state diffusion coefficient, D_L , for half of the interface adjacent to the liquid. Then, Eq.(8) reduces to BAKER's model[17]. Assuming a linear change of $\mu_B^0(\eta)$ and a constant $D_I(\eta)$ in the interface, Eq.(8) reduces to the vacancy trapping model of HILLERT et al[23]. Furthermore, a combination of smooth shape interface function for $\partial\mu_B^0(\eta)/\partial\eta$ and constant D_I assumption as the treatment of SVOBODA et al[22], or other treatments, for example truncated wedge interface[19–21], will lead to another solute trapping model.

However, the above treatments guarantee only a continuous but not smooth solute concentration profile across the interface to the bulk phases, i.e. the interface is not really continuous. In order to obtain a diffusive interface under steady state, the standard chemical potential μ_B^0 should change not only continuously but also smoothly from the interface to the bulk liquid. If $\partial\mu_B^0(\eta)/\partial\eta$ fulfills the following condition:

$$\partial\mu_B^0/\partial\eta|_{\eta=0} = \partial\mu_B^0/\partial\eta|_{\eta=1} = 0 \quad (9)$$

and also, if the diffusion coefficient D_I changes continuously from solid to liquid across the interface, then the steady-state interface diffusion function (i.e. Eq.(4)) will change continuously from the interface to the bulk liquid where there is no standard chemical potential gradient, i.e. the solute diffusion in the liquid and the interface can be described by a uniform formalism. By adopting a basic approach of the phase-field models[15], with defining the free energy density in the interfacial region, a simple expression for $\mu_B^0(\eta)$ is

$$\mu_B^0 = \mu_B^{S0} + (\mu_B^{L0} - \mu_B^{S0})[\eta^2(3-2\eta) + 3L\eta^2(1-\eta)^2] \quad (10)$$

where μ_B^{L0} and μ_B^{S0} are the standard chemical potentials of liquid and solid, respectively. The dimensionless parameter, L , which determines the characteristics of the interface, is assumed to be a constant value. Compared with phase-field models where the interface properties are dependent on the phase-field variable, ϕ , the interface properties in Eq.(10) are determined by the distance η . The term $\eta^2(3-2\eta)$ comes from the function $h(\phi)=\phi^2(3-2\phi)$, which is monotonic in the interface, and the term $\eta^2(1-\eta)^2$ comes from the double-well potential $g(\phi)=\phi^2(1-\phi)^2$ in the phase-field model[15].

Further, it is better that $\partial D_I(\eta)/\partial\eta$ fulfills the following condition below. To obtain a diffusive interface, such condition is not necessary under steady state condition, but it must be fulfilled under non-steady condition[24]:

$$\partial D_I/\partial\eta|_{\eta=0} = \partial D_I/\partial\eta|_{\eta=1} = 0 \quad (11)$$

Since it is assumed in the present model that $D_I(\eta)$ changes monotonic as a function of η , an expression for $D_I(\eta)$ is then obtained according to $h(\phi)=\phi^2(3-2\phi)$ in the phase-field model[15]:

$$D_I = D_S + (D_L - D_S)\eta^2(3-2\eta) \quad (12)$$

Until now, one can see that the interface shape function was deduced using phase-field approach[15] and the interface characteristic is described in terms of a double-well potential function with a dimensionless parameter, L .

Further, $\partial\mu_B^0(\eta)/\partial\eta$ can be obtained from Eq.(10) as

$$\frac{\partial\mu_B^0}{\partial\eta} = 6(\mu_B^{L0} - \mu_B^{S0})\eta(1-\eta)[1 + (1-2\eta)L] \quad (13)$$

Note that $\mu_B^{L0} - \mu_B^{S0} = RT_1 \ln k_e$, then substitution of Eqs.(10) and (13) into Eqs.(7) and (8) gives the following equations:

$$\begin{aligned} \frac{C(\eta)}{C_S} = & \left\{ \int_0^\eta \exp[\ln k_e[\eta^2(3-2\eta) + 3L\eta^2(1-\eta)^2]] + \right. \\ & \left. \int_0^\eta \frac{V\delta}{D_I(\eta)} d\eta \right\} \frac{V\delta d\eta}{D_I(\eta)} + 1 \Big/ \left\{ \exp[\ln k_e[\eta^2(3-2\eta) + \right. \\ & \left. 3L\eta^2(1-\eta)^2]] + \int_0^\eta \frac{V\delta}{D_I(\eta)} d\eta \right\} \end{aligned} \quad (14)$$

$$\begin{aligned} k = & \left\{ \exp[\ln k_e + \int_0^1 \frac{V\delta}{D_I(\eta)} d\eta] \right\} \Big/ \left\{ \int_0^1 \exp[\ln k_e[\eta^2(3-2\eta) + \right. \\ & \left. 3L\eta^2(1-\eta)^2]] + \int_0^\eta \frac{V\delta}{D_I(\eta)} d\eta \right\} \frac{V\delta d\eta}{D_I(\eta)} + 1 \end{aligned} \quad (15)$$

Now, a solute trapping model incorporating diffusive interface is obtained, as well as the solute composition profile is across the interface. Obviously, this is a relatively simple analytical expression, with characteristics analogous to phase-field approaches because the interface shape function is deduced from the defining the free energy density in the interfacial region of phase-field model[15] and the solute diffusion in the liquid and the interface can be also described by a uniform formalism, which is also the characteristic of the phase-field model. As shown in Eqs.(10) and (13), L is an important parameter, which plays an analogous role to E_B (i.e. the solute interaction energy at the center of the interface) from BAKER's solute trapping models[17], or to A (i.e. an additional potential term for determining the equilibrium interface characteristics) from the smooth interface model[22]. Under equilibrium condition, for an alloy with $k_e < 1$, if $-1 \leq L \leq 1$, the interface composition $C(\eta)$ increases continuously from C_S to C_L , and the

interface is defined as inert; if $L < -1$, $C(\eta)$ possesses a minimum value at $\eta = (1+L)/2L$, and the interface is defined as repulsive (i.e. a “repulsive force” occurs between the solute atoms and the interface); and if $L > 1$, $C(\eta)$ possesses a maximum value at $\eta = (1+L)/2L$, and the interface is defined as adsorptive (i.e. an “attractive force” occurs between the solute atoms and the interface). For an alloy with $k_e > 1$, however, the repulsive and adsorptive interfaces become prevalent for $L > 1$ and $L < -1$, respectively. As for the non-equilibrium behaviour of interface, a detailed discussion is presented elsewhere[24].

3 Model application

The present model was used to describe the solidification of Si-9%As (molar fraction) alloys. Fig.1 shows different model predictions, where the solid line is calculated with $D_L = 1.5 \times 10^{-9} \text{ m}^2/\text{s}$ [16], $D_S = 3 \times 10^{-13} \text{ m}^2/\text{s}$ [16], $k_e = 0.3$ [4], $\delta = 4.6 \times 10^{-9} \text{ m}$ and $L = 0.5$, within which δ and L are the fitting parameters. The predication of the phase-field model[16] with the parameter determining the thickness of the interfacial zone $\varepsilon = 3.5 \times 10^{-9} \text{ m}$, is shown as dashed line, while the predictions using Aziz's model with $V_{DI} = 0.68 \text{ m/s}$ and using Sobolev's model with $V_{DI} = 0.68 \text{ m/s}$ and $V_D = 2.6 \text{ m/s}$ are respectively imposed as the dotted line and the dashed-dotted line. Obviously, Aziz's model fits well the experiment data only at low and moderate velocities, i.e. $V < 1 \text{ m/s}$, Sobolev's model fits well the experiment data covering throughout the interface velocity range. Regarding the current model predictions, the steeper profile from the present model is relatively better than that from the phase-field model, in agreement with the experimentally measured partition coefficient for $V = 2 \text{ m/s}$. At low and moderate velocities, both model predictions almost coincide. Analogous to Aziz's model, an asymptotic convergence of the non-equilibrium

partition coefficient to one as $V \rightarrow \infty$ can be also described using the present model, whereas a sharp transition to $k = 1$ at $V = V_D = 2.6 \text{ m/s}$ is predicted using Sobolev's model (Fig.1). Compared with the phase field model[16], the current solute trapping model also incorporates the diffusive interface, but shows a relatively simple analytical expression.

4 Conclusions

1) By incorporating the diffusive interface into the solute drag treatment, a solute trapping model, with a simple analytical expression, is obtained.

2) When applying a basic approach defining the free energy density of the phase-field model, an interface shape function is introduced to derive the current model.

3) Both the standard chemical potential and the solute concentration change continuously across the interface, while the interface diffusion function holds continuously from the interface to the bulk liquid.

4) When applying the current model to Si-9%As (molar fraction) alloy with $L = 0.5$, a good prediction of the steeper profile for high interface velocity, which is analogous to the phase-field model predictions of DANILOV and NESLTER, has been obtained.

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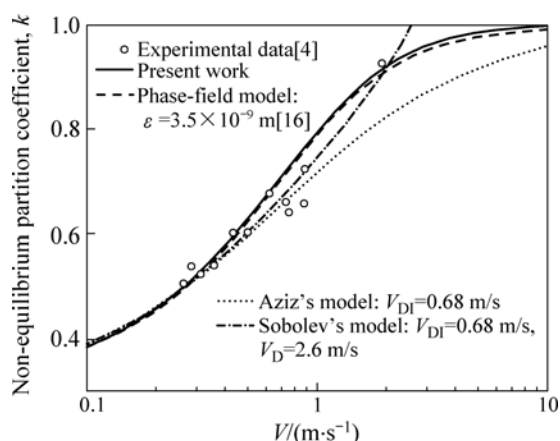


Fig.1 Partition coefficient k as function of interface velocity V for Si-9%As alloys

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