

Driving force for binary alloy solidification under far from local equilibrium conditions

S.L. Sobolev

Institute of Problems of Chemical Physics, Academy of Sciences of Russia, Chernogolovka, Moscow Region 142432, Russia

Received 23 March 2015; revised 17 April 2015; accepted 17 April 2015

Abstract—In this study we have incorporated the local nonequilibrium term into the Gibbs equation to obtain the local nonequilibrium correction to the driving force for solidification of binary alloys. The local nonequilibrium correction has been used to calculate the effective liquidus slope and the interface temperature for the model with and without solute drag effects. It has been demonstrated that both the local nonequilibrium correction and the solute drag play the most important role in the intermediate range of the interface velocity V . When V increases up to V_D , where V_D is the characteristic diffusive velocity, a sharp transition to completely diffusionless and partitionless solidification occurs, which implies that the local nonequilibrium correction and the solute drag effects can be ignored. The transition is accompanied by a sharp change in the effective liquidus slope and the interface temperature as functions of interface velocity. The model was applied to describe initial transient and steady-state solidification of Si–As alloy and a good agreement between the model predictions and the available experimental data was obtained.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Rapid solidification; Binary alloys; Gibbs energy; Liquidus; Extended thermodynamics

1. Introduction

In the past few decades, modeling of rapid solidification and solute trapping has gained attention for its role in many modern solidification processes such as thermal spraying, spin coating, and laser melting [1–3]. At deep undercooling the solidification process involves extremely fast heat and mass transfer at very small time and length scales, which implies that the process occurs under far from equilibrium conditions [3–30]. In such a case the classical thermodynamics cannot be applied due to violation of the local-equilibrium hypothesis and the local-nonequilibrium theory should be used. The most popular version of the local-nonequilibrium thermodynamics is the so-called extended irreversible thermodynamics (EIT) [31], which includes dissipative fluxes in the set of independent variables. Review of some other local nonequilibrium approaches can be found in [6,7,20,32–35]. It is remarkable that all the extended approaches lead to a hyperbolic diffusion equation as the simplest generalization of the classical diffusion equation of parabolic type to the local nonequilibrium case. The local-nonequilibrium transfer equation of hyperbolic type has been used to describe traveling waves of phase transformations under far from local equilibrium conditions [6]. This approach has been successfully applied to rapid solidification of binary alloys [8–12]. It has been demonstrated that the local nonequilibrium diffusion effects

are responsible for a sharp transition from diffusion controlled to diffusionless solidification with complete solute trapping at a finite interface velocity [8–12]. In recent years the local nonequilibrium diffusion approach has been extended to study different types of solute trapping models [13–16], rapid colloidal solidification [17], non-equilibrium dendrite growth [18,29,30], multicomponent alloy solidification [19], space nonlocal effects due to diffusion-stress coupling in liquid phase [20,21], solute drag effects [23–26], morphological stability [27,28], nonlinear liquidus and solidus [23,27,29,30]. The interface velocity V is related with the kinetic driving force for the interface motion ΔG through the reaction rate theory as

$$V = V_0[1 - \exp(-\Delta G/RT)] \quad (1)$$

where ΔG is the free energy change per mole between the solid and liquid phases, i.e. the driving force for solidification, R is the gas constant, T is the interface temperature, V_0 is the interface velocity at an infinite driving force. Under local nonequilibrium condition ΔG can be represented as [10,36]

$$\Delta G = \Delta G^0 + \Delta G^{neq} \quad (2)$$

where ΔG^0 is the local equilibrium part of the Gibbs free energy change, which can be calculated using classical irreversible thermodynamics, and ΔG^{neq} is the local nonequilibrium correction to the Gibbs free energy change, which arises due to local nonequilibrium effects and should be calculated on the basis of EIT [31]. The additional term, ΔG^{neq} ,

E-mail: sobolev@icp.ac.ru

was taken into account for calculation of the effective liquidus slope [26], which has been widely used in theoretical modeling of rapid alloy solidification but some uncertainties exist [23,27–30]. In this paper we calculate the local nonequilibrium correction to the change in free energy of transformation during rapid alloy solidification using EIT approach. We also calculate the effective liquidus slope and the interface temperature with allowance for the local nonequilibrium and solute drag effects and compare the model prediction with available experimental data.

2. Local nonequilibrium thermodynamic functions

2.1. Local nonequilibrium entropy and free energy for binary system

The local nonequilibrium Gibbs equation for binary system is [31]:

$$Tds = du + pd\rho^{-1} - \mu dC - \tau a\rho^{-2}D^{-1}JdJ \quad (3)$$

where T is temperature, s is a local specific entropy, C is concentration of component 1, $a = \partial\mu/\partial C$, $\mu = \mu_1 - \mu_2$, μ_i is chemical potential of component, τ is relaxation time to local equilibrium of the diffusion flux J , D is diffusion coefficient, ρ is mass density, p is pressure, u is specific internal energy. The local nonequilibrium correction to the classical Gibbs equation is represented by the last term in Eq. (3), which arises due to the diffusion flux J and depends on its relaxation time to local equilibrium τ . If the characteristic time of the process $t_0 \gg \tau$, the nonequilibrium correction is small and can be ignored. In this case Eq. (3) reduces to the classical (local equilibrium) Gibbs equation. Far from local equilibrium $t_0 \sim \tau$ and the nonequilibrium correction should be taken into account. Integration of Eq. (3) allows one to obtain the local nonequilibrium Gibbs free energy G in the form [31]

$$G = G^0 + G^{neq}$$

where G^0 is the local-equilibrium Gibbs free energy, and G^{neq} is the local non-equilibrium correction, which is given as

$$G^{neq} = J^2 \frac{\tau}{2D\rho^2} \left(\frac{\partial\mu}{\partial C} \right) \quad (4)$$

The local nonequilibrium entropy can be written in the analogous form:

$$S = S^0 + S^{neq}$$

$$S^{neq} = -J^2 \frac{\tau}{2D\rho^2 T} \left(\frac{\partial\mu}{\partial C} \right)$$

2.2. Local nonequilibrium correction to the driving force for solidification

The local nonequilibrium correction to the driving force for solidification in Eq. (2), ΔG^{neq} , is the difference between the local nonequilibrium correction to the Gibbs free energy in the liquid (L) G_L^{neq} and in the solid (S) G_S^{neq} . Using Eq. (4) one can obtain

$$\Delta G^{neq} = J_L^2 \frac{\tau}{2D} \left(\frac{\partial\mu}{\partial C} \right) - J_S^2 \frac{\tau_S}{2D_S} \left(\frac{\partial\mu_S}{\partial C_S} \right)$$

Taking into account that the solute diffusion flux in the solid phase is very small in comparison with that in the liquid phase, the nonequilibrium corrections for the driving force for solidification at the interface can be written as

$$\Delta G^{neq} = J_L^2 \frac{\tau}{2D} \left(\frac{\partial\mu}{\partial C} \right) \quad (5)$$

Note that all the parameters in these expressions refer to the liquid phase. Thus the local nonequilibrium driving force for solidification and the entropy change at the interface of binary mixture take the form

$$\Delta G = G_L - G_S = \Delta G^0 + J_L^2 \frac{\tau}{2D} \left(\frac{\partial\mu}{\partial C} \right) \quad (6)$$

For ideal solution Eq. (5) reduces to

$$\Delta G^{neq} = \tau RTJ_L^2/2DC_L \quad (7)$$

The mass balance law leads to the following interface condition

$$V(C_L - C_S) = J_L - J_S \quad (8)$$

where V is interface velocity. Taking into account that J_S is much smaller than J_L , Eq. (8) gives $J_L = VC_L(1 - K)$, where $K = C_S/C_L$ is solute partition coefficient. Substituting this expression for J_L in Eq. (7), we obtain the nonequilibrium corrections to the Gibbs free energy change:

$$\Delta G^{neq} = C_L RT(1 - K)^2 V^2 / 2V_D^2 \quad (9)$$

where $V_D = (D/\tau)^{1/2}$ is the characteristic diffusion velocity [8–10]. Thus the total Gibbs free energy change at the interface during rapid alloy solidification with allowance for the local nonequilibrium effects is given as

$$\Delta G/RT = \Delta G^0/RT + C_L(1 - K)^2 V^2 / 2V_D^2 \quad (10)$$

2.3. Steady-state regime

The exact mathematical treatment of the rapid alloy solidification problem may be found by solving the time-dependent governing equations, subject to appropriate initial and boundary conditions. But to avoid mathematical difficulties the steady-state approximation is usually used. The steady-state assumption assumes that after a short initial transient period the solid–liquid interface begins to move with constant velocity and the solute concentration is time-independent in the reference frame attached to the interface. Steady-state assumption significantly simplifies the mathematical formulation of the problem. Strictly speaking, the mathematical analysis shows that steady-state solidification takes an ‘infinite’ amount of time and distance to be achieved [1]. The local nonequilibrium approach gives the estimate of the characteristic time t_{st} to achieve steady-state as follows [22]:

$$t_{st}^{LNDM} = \gamma D(1 - V^2/V_D^2)/KV^2; \quad V < V_D \quad (11)$$

here γ is a constant such as at $t = t_{st}$ the interface solute concentration in the liquid is about 70% and 90% of the steady state concentration for $\gamma = 1$ and $\gamma = 2$, respectively [1]. When $V \geq V_D$, alloy solidification occurs in the diffusionless regime, which implies that $t_{st}^{LNDM} = 0$. Eq. (11) implies that the local nonequilibrium effects shrink the initial transient period in binary alloy solidification and for many practical situations, especially at high interface

Download English Version:

<https://daneshyari.com/en/article/1445245>

Download Persian Version:

<https://daneshyari.com/article/1445245>

[Daneshyari.com](https://daneshyari.com)