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Numerical description for the recalescence of bulk-undercooled $Cu_{70}Ni_{30}$ alloy

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ABSTRACT

Assuming thermal balance and solute conservation, a numerical model has been proposed to describe the recalescence behavior of bulk-undercooled Cu–Ni melts. Applying a finite-difference scheme, the transformed solid fraction upon recalescence is given as a function of the liquid temperature, while the average liquid concentration can be tracked by calculation of the liquid/solid (L/S) Gibbs energy difference, in combination with a dendrite growth model. Accordingly, a transition from non-equilibrium to equilibrium process has been described from the evolution of L/S Gibbs energy difference. Applying the present model, the experimentally observed maximum recalescence temperature can be well predicted.

1. Introduction

Non-equilibrium solidification plays an important role in the development of new materials and modification of traditional materials [1–3]. During the past decades, two methods, i.e., rapid quenching and bulk undercooling, have been widely applied to this fundamentally interesting and technologically important field [4–9]. Compared with the former case by rapid heat transfer from the melt to environment, the undercooling approach (e.g. melt fluxing, electromagnetic levitation) is, from the thermodynamic view, advantageous for in-situ agnostics, so as to understand the physical mechanisms underlying such rapid transformation process [9].

As for solidification of undercooled melts, recalescence behaves as an abrupt rising of liquid temperature due to the rapid release of latent heat, which accompanies the whole non-equilibrium solidification and decides the fraction of the as-formed solid. If the initial undercooling (ΔT) is less than the hyper-cooling limit, a plateau is then observed in the profile of temperature versus time, in which the residual liquid solidifies according to a near-equilibrium mode [10,11]. This implies that a borderline exists between the non-equilibrium and the near-equilibrium processes, which is essential for a precise description for solidification of undercooled melts. In order to determine the borderline between these two different solidification modes, it is thus inevitable to study the recalescence behavior as well as the maximum recalescence temperature T_R.

In the present paper, it is aimed to develop a mathematically simple but physically realistic model to describe the detailed recalescence behavior for Cu–Ni solid solution alloy, i.e., the evolutions of temperature and concentration of the residual liquid, which in turn determine the change of Gibbs free energy difference between liquid and solid, as well as the maximum recalescence temperature T_R.

2. Mathematical model

The present model is developed on the basis of a microscopic dendrite growth theory [12] and is further applied to describe the recalescence by assuming the phenomenological heat balance and solute conservation. Upon transformation, the release of latent heat increases the melt temperature, which thus decreases the thermodynamic driving force, and, in turn, the interface migration rate [12]. Owing to the concentration difference between liquid

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and as-formed solid, the solid concentration formed in each time interval during recalescence can be calculated according to the solute trapping model, while the concentration of residual liquid can be tracked from the conservation of solute atoms.

2.1. Heat flow balance

As for a spherical metallic sample undergoing solidification, where an uniform temperature is assumed and the change of phase density and heat capacity is neglected, the following equation can be formulated according to the heat flow balance, which considers heat capacity, the release of latent heat and the heat transfer to environment together [1,13,14]

$$\frac{\partial T}{\partial t} = -\frac{Q}{\rho c} + \frac{\Delta H}{\rho c}\frac{\partial f}{\partial t} \tag{1}$$

where f is the solidified fraction, T the melt temperature, ΔH the latent heat of solidification, Q (=$\rho c\Phi$) the heat extraction rate due to radiation and convection with ρc as the volume heat capacity and Φ as the cooling rate.

Generally speaking, recalescence proceeds faster in solid solution than that for eutectic or peritectic system. As reported earlier, the recalescence time for pure metal or solid solution alloy varies between 0.001 and 0.01 s [15,16], which is much less than that for eutectic system at the same undercooling (e.g. in Ni–Sn eutectic alloy [17], this value is about 0.1 s). Assume the cooling rate Φ measured experimentally as about 14 K/s [14], the decrease of temperature owing to heat extraction to the environment can be estimated as 0.1 K, which is nearly three orders lower than the rise of temperature due to release of latent heat to undercooled melt upon recalescence of Cu–Ni solid solution alloy. Analogous to the treatment in previous studies [13,17], it is reasonable to assume an adiabatic recalescence to minimize the computational requirements, and then Eq. (1) can be rewritten as

$$\frac{\partial T}{\partial t} = \frac{\Delta H}{\rho c}\frac{\partial f}{\partial t}. \tag{2}$$

The above equation can be further expressed as a discrete equation

$$f_{i+1} - f_i = \frac{\rho c}{\Delta H}(T_{i+1} - T_i) \tag{3}$$

where f_i and f_{i+1} are the transformed solid fraction corresponding to the melt temperature at T_i and T_{i+1}.

2.2. Dendrite growth rate in undercooled liquid

The growth of unconstrained dendrite in undercooled melts has been studied by many researchers and various models have been proposed to predict the interface migration rate V as a function of ΔT [18–29]. Generally, the framework of each model consists basically of the treatment for interface response function and the analysis of operation point for dendrite tip radius. The former one relates the total undercooling, ΔT, to four independent components, i.e., heat undercooling ΔT_t, solute undercooling ΔT_c, curvature undercooling ΔT_R and kinetics undercooling ΔT_k, respectively.

Considering further the effect of nonlinear liquidus and solidus, as well as the relaxation effect [25–29], Wang and Liu et al [12] have recently developed an extended dendrite growth model, where the interface response function can be given as

$$C_S^{eq}(T_i + \Delta T_R) - C_L^{eq}(T_i + \Delta T_R) + \frac{V}{V_0} + C_L^* N(V, T_i + \Delta T_R) = 0 \tag{4}$$

with

$$N(V, T_i + \Delta T_R) = 1 - k + \ln k/k'_0 + \frac{V}{V_D}(1-k)^2, \quad V < V_D \tag{5}$$

$$N(V, T_i + \Delta T_R) = -\ln k'_0, \quad V \geqslant V_D \tag{6}$$

where $C_L^{eq}(T_i+\Delta T_R)$ and $C_S^{eq}(T_i+\Delta T_R)$ are the equilibrium concentrations in the liquid and solid subjected to the curvature correction, V is the interface migration rate, V_D is the bulk liquid diffusion speed and V_0 is the upper limit of the interface advancement. C^*_L is the non-equilibrium concentrations in liquid at the interface corresponding to the interface temperature T_i, k and k'_0 are the non-equilibrium and equilibrium segregation coefficient subjected to the curvature correction. In order to determine the unique set of V and ΔT, the marginal stability analysis is further needed to analyze the dendrite tip radius, which can be given as

$$R = \frac{\Gamma}{\sigma^*}\left(\frac{P_T \Delta H}{C_P}\xi_L + \frac{2M(V, T_i + \Delta T_R)P_C C_L^*(k-1)}{\psi}\xi_C\right)^{-1}, \quad V < V_D \tag{7}$$

$$R = \frac{\Gamma}{\sigma^*}\left(\frac{P_T \Delta H}{C_P}\xi_L\right)^{-1}, \quad V \geqslant V_D \tag{8}$$

where

$$\xi_C = 1 - \frac{2k + 2M(V, T_i + \Delta T_R)C_L^* \partial k/\partial T|_{T=T_i+\Delta T_R}}{\sqrt{1 + \psi(\sigma^* P_C^2)^{-1}} + 2k - 1 + 2M(V, T_i + \Delta T_R)C_L^* \partial k/\partial T|_{T=T_i+\Delta T_R}}, \quad V < V_D \tag{9}$$

$$\xi_C = 0, V \geqslant V_D \tag{10}$$

$$\xi_L = 1 - \frac{1}{\sqrt{1 + (\sigma^* P_T^2)^{-1}}} \tag{11}$$

$$M(V, T_i + \Delta T_R) = \frac{-m_L(T_i + \Delta T_R)m_S(T_i + \Delta T_R)N(V, T_i + \Delta T_R)}{m_L(T_i + \Delta T_R) - m_S(T_i + \Delta T_R) + m_L(T_i + \Delta T_R)m_S(T_i + \Delta T_R)C_L^*(\partial N(V, T_i + \Delta T_R)/\partial T|_{T=T_i+\Delta T_R})} \tag{12}$$

where R is the dendrite tip radius, Γ is the Gibbs–Thompson coefficient, σ^*=1/4π^2 the stability constant, P_C=$VR/2D$ the solutal Peclet number, D is the liquid diffusion coefficient, P_T=$VR/2\alpha_L$ the thermal Peclet number, α_L the thermal diffusivity of liquid, m_L and m_S the slope of liquidus and solidus and ψ=1−V^2/V_D^2. The detailed description for the dendrite growth model is available in [12]. Strictly speaking, the solvability theory, which considers the anisotropy for surface energy, should be introduced to predict a correct shape of dendritic tip [21–24]. Yet, regarding the quantitative agreement between the calculated growth rate using marginal stability criterion and the experiment results (see following Section 3.1), this effect is neglected in the present study for the sake of simplicity.

2.3. Solute trapping model and solute conservation

It has long been known that local equilibrium is not applicable in the case of rapid solidification, and the segregation coefficient $k(V)$ (the ratio of solute concentration in the solid to that in the liquid) deviates from its equilibrium value k_0 to unity at sufficiently high interface migration velocity [30]. For non-equilibrium solidification subjected to the relaxation effect, a solute trapping model has been proposed by Sobolev [26,27], and is further corrected by the curvature effect as [12]

$$k(V) = \frac{V/V_{DI} + k'_0(1 - V^2/V_D^2)}{V/V_{DI} + 1 - V^2/V_D^2}, \quad V < V_D \tag{13}$$