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Investigation on recalescence temperatures of deeply undercooled melts



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ABSTRACT

According to the theory of classic thermodynamics, any transformation is driven by the decrease of Gibbs free energy of the system. Solidification pertains to the first order transformation and obeys this basic law. The Gibbs free energy of the condensed phases of metals and alloys is closely related to the temperature and composition of the system. Thus we can describe rapid solidification process in a more precise way by using quantitative thermodynamic calculation. In combination with solidification kinetics theory, we calculated the evolution of the thermodynamic parameters during rapid solidification process. On this basis, we proposed a criterion for the end point of recalescence process and built a physical model for describing rapid solidification process and predicting recalescence temperatures of undercooled melts. Good agreement can be achieved between the present model prediction and experimental data.

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1. Introduction

From the perspective of kinetics, rapid solidification of undercooled melts is a first order transformation and can be divided in to three basic physical processes, i.e. nucleation, growth and impingement of crystals [1–3]. Crystal nuclei can form continuously due to the structure and composition fluctuations in bulk undercooled melts. Once the sizes of these nuclei exceed the critical size, a large number of nucleation events would occur and then the undercooled melt starts recalescence. Rapid solidification of undercooled melts is a spontaneous heat releasing process. In such conditions, the temperature and composition of the melt ahead of the liquid/solid interface would change with the increase of the solid fraction, which would influence the subsequent solidification kinetics and microstructural transformation process. Therefore, it appears especially important to use kinetic models to describe the kinetics of rapid solidification process. Effective kinetic description of solidification process is helpful for the researchers to describe the variation of solidification parameters, e.g. the recalescence temperatures of undercooled melts.

2. Experimental procedures

Ni-20 at%Cu alloy samples were prepared by in situ melting pure Ni pieces (99.9% purity) and pure Cu pieces (99.99 wt% purity) under the protection of argon (Ar) atmosphere in a vacuum chamber. Ni-20 at%Cu alloy samples have an 8 mm diameter and a height of 1 cm. A high purity quartz crucible containing the alloy sample was placed in the center of an induction coil. The melting process was conducted in the vacuum chamber. The experimental details are referred to Ref. [4]. The cooling curves of the melts were measured by an infrared pyrometer, which was calibrated with a standard PtRh30-/PtRh6 thermocouple, and possesses are relative accuracy of \pm 3 K and a response time of 5 ms.

3. Recalescence temperature

At the end moment of rapid solidification, the recalescence temperature of an undercooled melt will reach a maximum value. In the early researches, Walker [2] and Hindmarsh [5] observed in undercooled Ni and H₂o that the maximum recalescence temperatures T_R can reach the liquidus T_L . Thus, it is generally considered that T_R is T_L . However, in recent a large number of undercooling experiments [2–12], it is found that T_R cannot reach T_L . In order to predict T_R in a quantitative way, assuming that the recalescence process is in adiabatic conditions, Piccone [13] first suggested that T_R can be calculated from the perspective of equilibrium thermodynamic phase diagram.

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$$C_{S}f_{S} + C_{L}(1 - f_{S}) = C_{0}$$
⁽¹⁾

where C_S and C_L are the equilibrium compositions of liquid and solid phases at T_R . C_0 is the initial composition of the alloy. f_s is the solid fraction at T_R and can be expressed as

$$f_S^R = \frac{T_R - T_N}{\Delta H_f/C_P} \tag{2}$$

where ΔH_f is the molar fusion enthalpy of the alloy, T_N the nucleation temperature where solidification starts, molar fusion enthalpy of the alloy, C_P the molar thermal capacity. Generally, the recalescence time is very short and the amount of heat releasing during solidification is much larger than that dissipated to surrounding. Thus, the assumption that recalescence process is in adiabatic conditions made by Piccone is reasonable. However, there are weaknesses in Piccone's model. For example, the solid composition at T_R is calculated according to the equilibrium phase diagram is unreasonable, because the diffusion in solid is much slower than that in liquid and cannot reach the equilibrium composition.

Considering the weaknesses of Piccone's model, Vedovato [14] investigated the rapid solidification behavior of undercooled droplets in atomization experiment and suggested that T_R should be in the interval between the temperatures determined by Scheil equation and Lever rule, which can be

$$f_{S} = \frac{(T_{M} - T) - m_{L}C_{0}}{(T_{M} - T)(1 - k_{e})}$$
(3)

$$\frac{df}{dT} = \frac{-m_L C_0}{(1 - k_e)(T_M - T)^2}$$
(4)

and

$$f_{S} = 1 - \left(\frac{T_{M} - T}{T_{M} - T_{L}}\right)^{-\frac{1}{1-k_{e}}}$$
(5)

$$\frac{df}{dT} = \frac{-m_L C_0}{\left(1 - k_e\right) \left(T_M - T\right)^2}$$
(6)

According to the energy conservation law, the temperature of the system varies as

$$\frac{\partial T}{\partial t} = -\Phi + \frac{\Delta H_f}{\rho C_P} \frac{\partial f}{\partial t}$$
(7)

where ρ is density. Φ is cooling rate. Considering that f_s is a function of *T*, Eq. (7) can be rearranged as

$$\frac{\partial T}{\partial t} = -\Phi + \frac{\Delta H_f}{\rho C_P} \frac{\partial f}{\partial T} \frac{\partial T}{\partial t}$$
(8)

i.e.

$$\frac{\partial T}{\partial t} = \frac{\Phi}{\frac{\Delta H_f \, \partial f}{\rho C_P \, \partial T} - 1} \tag{9}$$

We can obtain expressions of $\partial f/\partial T$ according to Scheil equation and Lever rule. Then we can obtain the temperature curves by Scheil equation and Lever rule after substitution of $\partial f/\partial T$ into Eq. (9). According to the assumption made by Vedovato [14], T_R should be in the interval of the temperatures obtained by Scheil equation and Lever rule. Lever rule is used in equilibrium conditions, i.e. the solute can diffuse homogeneously in the solid phase. While Scheil equation is used under the assumption that the solute cannot diffuse in the solid phase. Obviously, these two cases represent two extreme conditions of solute diffusion in the solid phase respectively, which cannot happen in real conditions. Thus, T_R should be between the temperatures obtained by Scheil equation and Lever rule. Fig. 1 gives calculated temperature curves of undercooled Ni-20 at%Cu alloys by Scheil equation and Lever rule according to Vedovato's model. The physical parameters used in the calculation are listed in Table 1. Fig. 1 also gives the temperature curve of rapid solidification of Ni-20 at%Cu alloy with undercooling of about 110 K. It is clear that $T_{\rm R}$ is lower than that the prediction of Vedovato's model. The reason could be that both Scheil equation and Lever rule are mainly considering solute segregation, while during real rapid solidification process, lattice defects such as dislocations can be introduced into the rapidly formed crystals. There is stored energy due to these defects in the system, therefore the latent heat released during solidification will be decreased and this make T_R be lower than the prediction of the model.

Hindmarsh [5] investigated rapid solidification of undercooled melt and suggested that the composition of the residual liquid during recalescence had a strong influence of $T_{\rm R}$. Thus, if we can calculate the solid concentration during recalescence and the weakness in Piccone's model can be corrected.

The Gibbs free energy difference of the liquid and solid phases provides the driving force for transformation. Thus, accurate quantitative thermodynamic calculation can help us to comprehend the rapid solidification process better. As Ni-20 at%Cu alloy is a solid solution alloy, we can use the sub-regular model to calculate the Gibbs free energy of the phases

$$G^{j} = x_{Ni}^{0}G_{Ni}^{j} + x_{Cu}^{0}G_{Cu}^{j} + RT(x_{Ni} \ln x_{Ni} + x_{Cu} \ln x_{Cu}) + G_{ex}^{j}, \quad (j = L, S)$$
(10)

where x_{Ni} and x_{Cu} are molar fraction of Ni and Cu. ${}^{O}G_{Cu}^{j}$ and ${}^{O}G_{Ni}^{j}$ are standard chemical potential of Ni and Cu. G_{ex}^{j} is the excess free Gibbs energy. The driving force of transformation can be expressed as

$$\Delta G = G^L - G^S \tag{11}$$

where G^L and G^S are Gibbs free energy of liquid and solid phases respectively.

Using the thermodynamic parameters listed in Table 2, we calculated the Gibbs free energy variations of the liquid and solid phases of Ni-20 at%Cu alloys at temperatures of 1665 K, 1675 K, 1679 K and 1683 K respectively. 1665 K is the experimental maximum recalescence temperature. 1675 K and 1679 K is calculated by Scheil equation and Lever rule according to Vedovato's model [14]. 1683 K is the equilibrium liquidus temperature of Ni-20 at%Cu alloys.

As temperature increasing, the activity of atoms will enhance



Fig. 1. Cooling curves for Ni-20 at%Cu alloys with different solidification modes.

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