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Decomposition of crystal-growth equations in multicomponent melts

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ABSTRACT

Using a variational approach, the macroscopic laws of the growth of a new-phase, multicomponent particle are compared to the physicochemical laws of processes in the “new phase – initial melt” system. A suitable equation-based method has been developed to calculate the growth of a new-phase particle under the conditions of diffusion growth and non-equilibrium solute trapping by the quickly growing front of a new phase. The laws of crystal growth have been studied while annealing the amorphous alloy FINEMET® $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$.

1. Introduction

The elaboration of new, advanced materials stimulates the further development of methods for the mathematical modelling of crystal growth in multicomponent melts, making it possible to predict how the features of a technological process affect the characteristics of the obtained materials.

The solution of the crystal-growth equation faces substantial mathematical difficulties. The problem implies the analysis of interrelated physicochemical and hydrodynamic processes in a melt, the growing crystal particle and the interface between the two phases [1,2]. Along with traditional methods describing a phase interface of zero thickness, phase-field models are being developed [3]. The methodology of the transition layer is the basis of these methods. An additional parameter continuously describing the phase interface changing from zero to unity is applied. This parameter enables the continuous description of the system, avoiding mathematical problems at the interface (Stephan's problem). Phase-field methods are being actively developed and involve not only various tasks of crystal-growth-speed calculations but also make it possible to foresee the growing crystal morphology.

According to the classical theory, crystal growth implies local equilibrium at the interface of the growing crystal. Under non-equilibrium growth conditions dependent on the high velocity of the boundary transition, deviations from the local equilibrium conditions are possible. The first experiment confirming deviations from local equilibrium were performed by Baker and Cahn [4]. The result of the experiment is explained by a solute-trapping effect. If the speed of the surface transition grows and becomes equal to the speed of atomic diffusion, then impurity atoms lack the time to diffuse from the front and are overtaken by the solid phase. The first mathematical equations describing the process of solute trapping were developed by Aziz [5]. Subsequently, this domain has undergone dynamic development; a detailed review of related works is given in [1].

In the present article, a new method has been developed that is based on the combination of the classical thermodynamic approach for the description of a crystal-melt system with variational equations of analytical mechanics describing crystal as a macrobody.

2. Problem statement

The problem of multicomponent particle diffusion growth in a changing temperature field is under consideration. New-phase generation in the model is defined by interface-transition processes across the surface of the growing particle. This method is not limited to the system above but can be applied to other problems; for example, for the description of multifront growth problems, for which the derivation of the growth equations by means of common balance equations has considerable difficulties [6].

A number of assumptions, usually employed to create a model of crystal growth in metal melts, have been made in the article. Let us consider a particle growing in the multicomponent melt.

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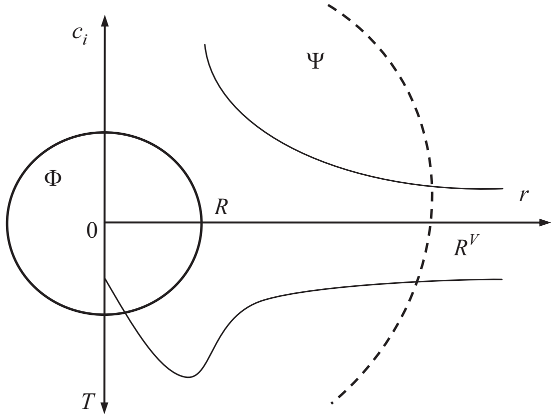

Fig. 1. The change in the melt-component concentration and temperature near the particle.

For simplicity, we assume a spherical coordinate system with its origin in the centre of the growing particle. Let R be the radius of the crystal (Fig. 1). Let us also assume that the distribution of parameters in the system is spherically symmetrical. For simplicity, we use the symbol $\Psi$for the melt phase and Φ for the particle.

Let m components $\mathfrak{R}_1^{\Psi},\mathfrak{R}_2^{\Psi},\ldots,\mathfrak{R}_m^{\Psi}$, n of which can be present in the growing crystal phase, be present in the solution. The particle growth is defined by n processes of interphase transition of components across its surface

$$\mathfrak{R}_i^{\Psi} \to \mathfrak{R}_i^{\Phi}, \quad i=1,\ldots,n. \tag{1}$$

The growth of the particle is specified by the thermal conductivity equations and the diffusion of components in the crystal and the melt, as well as by the heat-transfer and mass-transfer equations through the particle surface. The mass concentrations of the components c_i and the temperature T change during both phases (Fig. 1). Local gradients of temperature and composition appear near the particle surface. At a considerable distance from the particle, the surface concentrations and the temperature flatten and reach the mean values of the melt. This tendency is characteristic of the initial stage of the phase transition when the centres of origin are located at a considerable distance from each other.

3. Variational approach

Let us calculate several distances from the particle centre R^{ν}, for which the values of the concentrations and the temperature do not virtually change and their values are equal to the mean values of the melt (Fig. 1). We can speak about the isolation of a volume V, especially for a short period of time.

Setting aside the detailed physicochemical description, we consider the whole system as a macrobody. The particle is actually a macro-object growing in the initial melt. Taking the isolation of the system into account, we can allow for the particle growth to be characterised by two parameters only: the radius value R at the given moment of time t and the velocity of the radius change during time $\dot{R}$. Because any change in the system is characterised by the change of the chosen parameters, the entropy production can be given as a function of these parameters by $P=P\left(R,\dot{R},t\right)$. Within the bounds of our definitions to the function P, the Lagrange equation can be applied as follows[7]:

$$\frac{d}{dt}\frac{\partial P}{\partial \dot{R}}-\frac{\partial P}{\partial R}=0 \tag{2}$$

On the other hand, considering the collection of thermodynamic processes occurring in the system particle-initial melt, we write the following expression for the entropy production:

$$P=\int_{V^{\Phi}}\sigma^{\Phi}\,dV+\int_{V^{\Psi}}\sigma^{\Psi}\,dV+\int_{F^{\Phi}}\sigma^{F}\,dF, \tag{3}$$

where σ^{Φ}, σ^{Ψ} and σ^{F} are the intensities of the entropy production at the corresponding phases and the interface. The first term defines the entropy production in phase Φ, and the second term in phase Ψ, limited by a sphere of radius R^{ν}. The third integral takes into consideration the effects at the interface of Φ and Ψ.

For the intensities of the entropy production at the phases Φ andΨ, certain expressions are applied as follows [8]:

$$\sigma^{\Phi}=\boldsymbol{J}_q^{\Phi}\cdot\mathbf{grad}\left(\frac{1}{T}\right)-\frac{1}{T}\sum_{i=1}^{n}\boldsymbol{J}_i^{\Phi}\cdot\left[\mathbf{grad}\,\mu_i^{\Phi}\right]_T, \tag{4}$$

$$\sigma^{\Psi}=\boldsymbol{J}_q^{\Psi}\cdot\mathbf{grad}\left(\frac{1}{T}\right)-\frac{1}{T}\sum_{i=1}^{m}\boldsymbol{J}_i^{\Psi}\cdot\left[\mathbf{grad}\,\mu_i^{\Psi}\right]_T, \tag{5}$$

where for the respective phases $\boldsymbol{J}_i$ is the diffusion flux of ith component, $\boldsymbol{J}_q$ is the thermal flux, $\left[\mathbf{grad}\,\mu_i\right]_T$ is the gradient of the chemical potential of ith component, calculated for a constant temperature. The mass concentration is calculated as $c_i=\rho_i/\rho$, whereρ is the density, and ρ_i is the density of the ith component.

For the interface, we make use of the expression stated below, obtained for the case of a particle growing out of a multicomponent melt [9,10]

$$\sigma^{F}=\sum_{i=1}^{n}I_i\frac{A_i}{T}, \tag{6}$$

where $I_i \quad (i=1,\ldots,n)$ is the molar speed of product generation $\mathfrak{R}_i^{\Phi}$ per unit area of phase interface, $A_i=M_i(\mu_i^{\Psi}-\mu_i^{\Phi})$ is the affinity for interphase transition of the ith component at the boundary of the crystal-melt, and M_i is the molecular weight of ith component.

To transform Eq. (2), we must find the partial derivative of the entropy production with respect to the velocity change of a particle of radius $\partial P/\partial\dot{R}$. The variables σ^{Φ} and σ^{Ψ} define the phases Φ and Ψ, ex facte, and these variables do not depend on the velocity change of the radius. Thus, taking the independence of the variables into account, we can write as

$$\frac{\partial P}{\partial \dot{R}}=\int_{F^{\Phi}}\sum_{i=1}^{n}\frac{A_i\partial I_i}{T\,\partial \dot{R}}\,dF \tag{7}$$

In metal melts, the velocity of the interphase transitions (1) is limited by the diffusion-based supply of chemical agents. Such systems are considered to attain local equilibrium at the particle surface. Thus, the affinity of the interphase transition of the components possesses zero value on the particle surface:

$$A_i=0. \tag{8}$$

This uses assumption (8) that the entropy production P does not depend on the velocity change of the nucleus radius $\dot{R}$. Specifically, assumption (8) is the condition of the stability of Eq. (2).

$$\frac{d}{dt}\frac{\partial P}{\partial \dot{R}}=0 \tag{9}$$

And thus, from Eq. (2),

$$\frac{\partial P}{\partial R}=0\cdot \tag{10}$$

Analysing the results, we can draw an analogy to the Prigogine principle of minimum entropy production P [8,11]. When describing stationary states, Prigogine considered the conditions of independence from the time of the derivative of the function P with respect to one of the Onsager variables, which corresponds to zero of one of the fluxes in the phenomenological equation. In our equation, we have obtained the independence from the time of the derivative of the function P with respect to one of two variables specifying the state of the system. Thus, the assumption (8) of