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Acta Materialia 55 (2007) 5225–5235
Acta MATERIALIA
www.elsevier.com/locate/actamat

A phase-field model for non-equilibrium solidification of intermetallics

H. Assadi *

Tarbiat Modares University, Department of Materials Engineering, P.O. Box 14115-143 Tehran, Iran

Received 16 March 2007; received in revised form 4 May 2007; accepted 29 May 2007
Available online 16 July 2007

Abstract

Intermetallics may exhibit unique solidification behaviour—including slow growth kinetics, anomalous partitioning and formation of unusual growth morphologies—because of departure from local equilibrium. A phase-field model is developed and used to illustrate these non-equilibrium effects in solidification of a prototype B2 intermetallic phase. The model takes sublattice compositions as primary field variables, from which chemical long-range order is derived. The diffusive reactions between the two sublattices, and those between each sublattice and the liquid phase are taken as 'internal' kinetic processes, which take place within control volumes of the system. The model can thus capture solute and disorder trapping effects, which are consistent—over a wide range of the solid/liquid interface thickness—with the predictions of the sharp-interface theory of solute and disorder trapping. The present model can also take account of solid-state ordering and thus illustrate the effects of chemical ordering on microstructure formation and crystal growth kinetics.

Keywords: Non-equilibrium processes; Solidification; Intermetallics; Disorder trapping; Phase-field modelling

1. Introduction

Solidification of materials under non-equilibrium conditions, e.g., during rapid cooling, may result in unique microstructural and kinetic effects. In solidification of disordered solid solutions, for instance, large departures from local equilibrium may lead to solute trapping during crystal growth [1]. Solute trapping signifies a condition where the composition of the solid at the interface approaches that of liquid as the crystal growth velocity is increased. In solidification of intermetallics, solute trapping on two or more sublattices of the solidifying phase leads to the suppression of its chemical long-range order. This kinetic effect, known as disorder trapping, can in turn lead to generally slow solidification kinetics and, in some cases, to partitioning behaviour very different from that in the solidification of random solid solutions. Boettinger and Aziz [2] developed a sharp-interface model to illustrate solute and disorder trapping in intermetallics. This model was later used for quantitative analysis of solidification kinetics in real intermetallic forming systems [3–6]. However, interpretation of solidification microstructures in these systems has so far been limited to qualitative analyses.

In recent years, phase-field modelling has been used as a robust method for quantitative analysis of microstructure evolution. In this method, the entire microstructure is represented by one or more phase-field variables, which evolve (for instance) through minimization of a free energy functional. The method incorporates the build-up and movement of diffuse interfaces between different phases or grains, and thus eliminates the need for special algorithms for tracking internal moving boundaries. Originally used to simulate solidification microstructures [7], the phase-field approach has now been extended to model microstructural evolution in various processes, ranging from sintering [8] to electrochemical reduction of oxides [9].

Apart from their general formalism, various phase-field models may be characterized by the method they use to link field variables to one another at the corresponding phase boundaries. This concerns, in particular, the relationship between the composition variables at the solid/

* Tel.: +98 21 88011001; fax: +98 21 88006544.
E-mail address: ha10003@modares.ac.ir

1359-6454/$30.00
doi:10.1016/j.actamat.2007.05.042

liquid interface in alloy solidification. In the 'geometrical' approach, e.g., by Beckermann et al. [10], these variables are imposed upon the interface, after they are worked out from the equilibrium phase diagram and sharp-interface models of solidification. This approach allows for the modelling of solidification in systems of complex thermodynamics, without the need to use complex thermodynamic descriptions. Thus, the geometrical approach extends the scope of application of phase-field modelling to real systems of technological interest. However, this approach is limited to modelling solidification under local equilibrium conditions. In contrast, the set of composition variables at the interface is obtained as part of the solution in models using a Cahn–Hilliard formulation [11]. An interesting property of this formulation is that it allows one to illustrate non-equilibrium kinetic effects such as solute trapping [12–14] during solidification. However, the extent of solute trapping in the standard Cahn–Hilliard formalism depends on the thickness of the solid/liquid interface. Moreover, the existing phase-field models of non-equilibrium solidification focus mainly on binary systems where the solid phase is a random solid solution.

The present work aims to apply the phase-field approach to non-equilibrium solidification of chemically ordered intermetallic phases. The phase-field model presented in this work is to incorporate chemical long-range order and thus to illustrate the non-equilibrium effects associated with disorder trapping. The model also aims to incorporate solid-state chemical ordering. As a preliminary examination, the present model is applied to the solidification of simple prototype systems, including one resembling the Ni–Al system in the homogeneity range of the B2 (β) intermetallic phase. Numerical simulations are carried out for one-dimensional (1-D) and two-dimensional (2-D) solidification of the B2 phase in these model systems. The results of modelling are discussed with reference to the predictions of the sharp-interface modelling and to previous experimental observations.

2. Method

In the present analysis, the system is represented by five primary field variables as follows: the structural order (phase-field) parameter ϕ, the temperature T, the molar fraction of solute in liquid x_B^L, and those in the sublattices of a B2 intermetallic phase y_B^α and y_B^β. In case of multiple-grain solidification, an additional parameter θ is used to represent crystal orientation. The temporal evolution of these variables is worked out by solving appropriate equations of crystallization kinetics, heat transfer and diffusion. Two other field variables, namely, the solid composition x_B^S and the chemical long-range order parameter η are derived from the sublattice compositions as follows:

$$x_B^S = \frac{1}{2}\left(y_B^\alpha + y_B^\beta\right) \tag{1a}$$

$$\eta = y_B^\alpha - y_B^\beta \tag{1b}$$

Using sublattice compositions as prime field-variables eliminates the need to define multiple order parameters, e.g., when modelling anti-phase domains (APDs). It also eliminates the need to consider an additional energy barrier between such domains. Another prime assumption in the present model is that the solid/liquid interface is an inhomogeneous mixture of solid and liquid phases, as depicted schematically in Fig. 1. As will be shown later, this conjecture provides specific modelling capacities. It also appears to be consistent with the results of the atomistic simulations of the solid/liquid interface in metallic alloy systems [15]. According to this picture, the structural order parameter (ϕ) represents the fraction of solid in control volumes of the system. Thus, $\phi = 1$ and $\phi = 0$ represent solid and liquid, respectively. Accordingly, the overall composition x_B is obtained as the weighted-average of the solid and liquid compositions, i.e., $x_B = \phi x_B^S + (1-\phi)x_B^L$. Likewise, the overall chemical order parameter is obtained as the weighted-average of the chemical order in solid and liquid, which reduces to $\phi\eta$, assuming no chemical order in liquid. Moreover, diffusion of species in solid and liquid are treated by solving a generalized system of equations for the entire domain. As will be shown later, the system of equations assumes different forms for different regions, as signified by the value of ϕ.

2.1. Phase and orientation fields

The phase field evolves with time according to an Allen–Cahn formulation [16], where the rate of change of the phase-field parameter is given as

$$\frac{\partial\phi}{\partial t} = -M_\phi\left(\frac{\partial f}{\partial\phi} - \varepsilon_\phi^2\nabla^2\phi\right) \tag{2}$$

in which M_ϕ is the interface mobility, ε_ϕ is a constant, and f is the local free energy density, i.e., the free energy per unit volume of the solid/liquid mixture in the interfacial region. The local energy density is assumed to have the following form:

$$f = h_1 F_S + (1-h_1)F_L + h_2 W \tag{3}$$

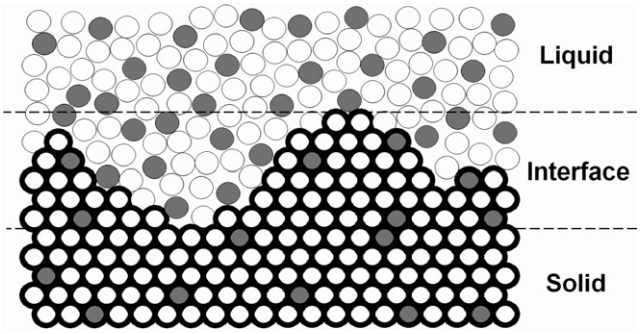

Fig. 1. A schematic depiction of the solid/liquid interface, showing the interfacial region as a 'mixture' of distinctive solid and liquid phases separated by 'sharp' boundaries.