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Phase-field modeling of coring during solidification of Au–Ni alloy using quaternions and CALPHAD input

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Abstract

A numerical method for the simulation of microstructure evolution during the solidification of an alloy is presented. The approach is based on a phase-field model including a phase variable, an orientation variable given by a quaternion, the alloy composition and a uniform temperature field. Energies and diffusion coefficients used in the model rely on thermodynamic and kinetic databases in the framework of the CALPHAD methodology. The numerical approach is based on a finite volume discretization and an implicit time-stepping algorithm. Numerical results for solidification and accompanying coring effect in a Au–Ni alloy are used to illustrate the methodology.

Keywords: Phase-field model; Alloy; Solidification; CALPHAD; Numerical method

1. Introduction

The microstructure of a material has a large influence on its mechanical properties. An important computational tool to simulate microstructure formation and evolution is the phase-field model (for a review, see e.g. [1,2]). In phase-field modeling (PFM), the basic variable is a phase variable which takes a specific value for each phase present in the simulation. Transition regions between phases are described by a smoothly varying value of that phase variable (diffuse interface) such that the complete field can be easily discretized using an appropriate numerical method. While this approach is used typically for two phases (e.g. solid and liquid), more phase variables can be added to describe additional phases, or to distinguish grains of different orientations (multi-phase-field model). Other fields may include alloy composition, temperature, local elastic deformation, etc. PFM is a phenomenological approach, and its parameterization determines bulk energies of each phase as a function of all the variables included in the model, as well as interface energies that may depend in particular on misorientation between two adjacent grains. It is important to provide a realistic parameterization of such models if one expects to gain insights into material properties. This is the reason why various recent research efforts in the field targeting alloy properties have been coupling PFM approaches to a physical database to include known thermodynamic and kinetic properties. To provide a realistic thermodynamic description of all phases in a material, Grafe et al. proposed to employ thermodynamic data from databases according to the CALPHAD method [3] for the multicomponent extension to PFM. They used interfaces to the Thermo-Calc and DICTRA software to calculate Gibbs energies, chemical potentials and diffusion matrices. Zhu et al. [4] used the CALPHAD method to construct the local free energy in the Cahn–Hilliard equations.

As an alternative to using a very large number of phase-field variables to describe many grains of many different orientations in multi-phase-field models, various models representing the local crystallographic orientation and its

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evolution in time were introduced (orientation-field methods). Our model is closely related to the one introduced by Pusztai et al. [5]. Instead of a multi-phase-field model, we use a quaternion to describe the local grain orientation in a crystal. We extend our recent work on this model [6] to include modeling of alloys with composition-dependent diffusion coefficients and free energies parameterized using the CALPHAD methodology. Composition-dependent diffusion coefficients are calculated following the formulation proposed by Andersson and Agren [7]. We use the formulation proposed by Eiken et al. [8] for the time-evolution composition equations. Our treatment of binary alloys at interfaces is based on the model proposed by Kim et al. [9]. We assume a diffusion-controlled time evolution. For simplicity, anisotropy effects are neglected, but crystal symmetries are taken into account. We limit our study to a binary alloy, but the methodology is quite general and can be applied directly to general multicomponent alloys.

We apply our methodology to the study of coring in Au–Ni alloys. Using an efficient parallel implementation of an implicit time-stepping algorithm, we are able to study the time evolution of grain coarsening over a relatively long time scale. To validate our model and verify our implementation, we compare one-dimensional results to those from DICTRA (diffusion-controlled transformation) software [10,11].

2. Coring in binary alloys

Since the conditions of "equilibrium" transformation are in practice rarely realized because of the role of kinetics in readjusting phase compositions during a transformation at each temperature increment, a so-called coring phenomenon occurs, characterized by the development of compositional gradient within grains. This is a general phenomenon that has been observed for more than a century in liquid–solid transformations with the prototypical example of freezing in Cu–Ni, and also in solid–solid phase transformations, as soon as the rates of diffusion in the two phases involved in the transformation are different [12]. In a liquid–solid transformation, since the rate of diffusion in the solid phase is always much lower than in the liquid phase, coring cannot be avoided, and homogeneous equilibrium is for practical purposes only maintained in the liquid state. Let us consider a portion of the equilibrium phase diagram for a binary Au–Ni alloy, which is the alloy selected for the present study, characterized by liquidus and solidus lines delineating a two-phase liquid (L) + face-centered cubic (fcc) (F) region as shown in Fig. 1.

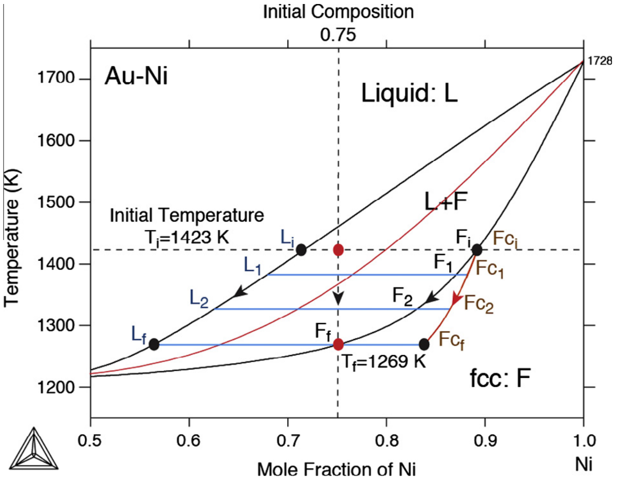

Fig. 1. Coring between the liquid state and the fcc phase in Au–Ni alloys. The red line located in the two-phase region represents the T_0 curve associated with equal Gibbs energies for the two phases, liquid and fcc. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In the present example homogeneous equilibrium is maintained in the L phase but not in the F phase since the rate of diffusion is much lower in the solid phase F, i.e. $D_L \gg D_F$. Under equilibrium conditions, let us consider an alloy of nominal composition AuNi$_3$ fully equilibrated at $T_1 = 1423$ K with a proportion of L (L_i) and F (F_i) phases according to the lever rule. The F phase takes from the L phase a disproportionately large amount of the Ni component, causing the L phase to become richer in Au as compared with the nominal alloy composition. As temperature decreases, the trajectories of the composition field for the L and F phases evolve along the (black) lines indicated by single arrows in Fig. 1. As the temperature is lowered, $T_i > T_1 > T_2$, the L phase becomes richer in Au species and the F phase must also move toward higher Au content. This can only happen by an increase in solid fraction (which contains more Ni than liquid at equilibrium), the preferential adsorption of Au from the L phase and the diffusion of Au species into the F phase formed previously at higher temperature. Because of the strong adjustment in composition in the two phases that needs to occur, departure from equilibrium is to be expected when ordinary cooling rates are used. At the last temperature T_f that indicates the bottom of the two-phase region at the nominal composition AuNi$_3$, at about 1269 K, the F phase is richer in Ni than at equilibrium, and because of the slow diffusion within the solid phase, a gradient of composition within each F develops with a higher Ni-content than the equilibrium composition in the center of the grains. Hence a cored structure (i.e. exhibiting a gradient of composition) develops inside the F grains with an average composition that evolves along the red line (associated with Fc labels) in Fig. 1, whereas the L matrix is compositionally homogeneous.

Hence, the coring leads to the existence of a Ni-rich (Ni-poor) region in the center (at the edge) of each F grain region that grows in the L matrix as soon as the alloy enters the two-phase region. Because grain growth develops at a different rate than species diffusion, the coring structure is retained in the single-phase field in the region of stability of the F phase. To achieve homogenization, the F phase of Au–Ni has to be annealed at a temperature that does not significantly alter the grain morphology and grain-size distribution (which are both required for engineering applications), and at the same time at a temperature high