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Phase-field method and Materials Genome Initiative (MGI)

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Abstract Predicting and controlling the microstructure evolution within a material are considered as the "holy grail" of materials science and engineering. Many important engineering materials are designed by controlling their phase transformations and microstructure evolution. Examples include the improvement of mechanical properties through solid-state precipitation reactions in Ni-based superalloys and age-hardened Al alloys, the useful dielectric properties and electro-mechanical coupling effects by manipulating the phase transitions in ferroelectric crystals, and the memory effect of shape-memory alloys by utilizing martensitic transformations. Phase-field method has become the method of choice for modeling three-dimensional microstructure evolution for a wide variety of materials processes. This short article briefly discusses the potential roles that phase-field method can play in the Materials Genome Initiative.

Keywords Materials Genome Initiative · Phase field · Microstructure

In the summer of 2011, US President Obama announced the Materials Genome Initiative (MGI) for Global Competitiveness [1]. This new initiative calls for major efforts to significantly advance three areas of research: multiscale computational materials science, open source cyber infrastructure for data management, and an integrated approach combining computation and experiments to accelerate the development of advanced materials. In one of the paragraphs in the announcement [1], it states that "The ultimate goal is to generate computational tools that enable real-world materials development, that optimize or minimize traditional experimental testing, and that predict materials performance under diverse product conditions. An early benchmark will be the ability to incorporate improved predictive modeling algorithms of materials behavior into existing product design tools. For example, the crystal structure and physical properties of the materials in a product may change during the product's processing, due to varying conditions. It could be disastrous to the performance of a product if, for instance, the tensile strength of its bolts changed during manufacture. The ability to model these morphology and property changes will enable faster and better design."

The structure and morphology changes in the above paragraph refer to the phase transformation and microstructure evolution of a material in the field of materials science and engineering. A microstructure may contain a wide variety of structural features such as phases of different compositions and/or crystal structures, grains of different orientations, domains of different structural variants, domains of different electrical or magnetic polarizations, as well as structural defects such as interphase boundaries, grain boundaries, twin walls, cracks, surfaces, and dislocations. The length scales of these structural features range from nanometers to microns.

Microstructures evolve during materials processing or in service as a result of phase transformations, chemical reactions, and/or particle or domain coarsening. The common processing variables are temperature, composition, and heating/cooling rates. Microstructures may also evolve under the influence of external fields such as an applied

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stress or electrical or magnetic field. The time scale for microstructure evolution in materials may span from a fraction of a second to days or even months or years. One of the main goals for materials design is to capture the optimum microstructures having the most desirable properties and to minimize its degradation in service.

Finding an optimum microstructure for the desirable properties requires lengthy and costly experimentations in the processing parameter space of temperature, composition, and time. As stated in the MGI announcement, "This new integrated design continuum—incorporating greater use of computing and information technologies coupled with advances in characterization and experiment—will significantly accelerate the time and number of materials deployed by replacing lengthy and costly empirical studies with mathematical models and computational simulations [1]."

Phase-field method is a powerful computational method for predicting the microstructure evolution in a wide variety of materials processes [2–5]. In a phase-field model, a set of continuous fields are employed to represent a microstructure. They are typically uniform inside a phase or domain and sufficiently far away from the interfaces or walls. The field variables have the same uniform values in the same phase or the same types of domains within a given microstructure. Different values of the field variables, for example, 0 and 1, distinguish different phases or domains. Across the interfaces between different phases or domains, the field variables vary continuously from one uniform value corresponding to one type of phase or domain to another uniform value corresponding to another phase or domain. Therefore, the interfaces in a phase-field model are diffuse and possess a certain thickness.

Field variables can be either conserved or non-conserved, depending on if they satisfy the local conservation law, $\partial\varphi/\partial t = -\nabla \cdot \boldsymbol{J}$, where ϕ is a field variable and $\boldsymbol{J}$ is the corresponding flux. For example, composition field is conserved, while long-range order parameter fields describing ordered domain structures are non-conserved. It is easy to understand that the artificial phase field in solidification modeling of a single-component liquid is non-conserved, since its value can go from 0 to 1 for the whole system. Conserved and non-conserved variables require different kinetic laws for their evolution as discussed below.

Field variables can be physical or artificial. Physical fields refer to well-defined order parameters which can be experimentally measured. The interfacial width described by a physical field is also expected to reflect the actual interfacial width in a microstructure. In phenomenological theories of phase transformations, order parameters are used to characterize the nature and the critical temperatures of phase transformations which produce the microstructures. A well-known example is the long-range order parameter for order–disorder transformations. The corresponding order parameter field can be employed to describe the antiphase domain structures resulted from ordering. Another example is a composition field which describes a two-phase microstructure with differences in compositions between the two phases. A composition field is also sufficient to describe the morphological evolution during phase separation through either nucleation and growth or spinodal decomposition or during precipitate coarsening in a binary alloy. Other examples of physical order parameters include electric polarization for a ferroelectric phase transition and magnetization for a ferromagnetic phase transition. On the other hand, artificial fields are introduced for the sole purpose of avoiding tracking the interfaces during a microstructure evolution. Essentially all phase-field models of solidification employ an artificial field called the "phase field". The interfacial width described by artificial fields has no direct relation to the physical width of a real interface. The thermodynamic and kinetic coefficients in the phase-field equations are chosen to match the corresponding parameters in the conventional sharp-interface equations through sharp- or thin-interface analyses [3].

Many examples of microstructures require more than one type of order parameters. For example, precipitation of an ordered intermetallic phase in a disordered matrix, a fundamental process in many technologically important alloy systems such as Al alloys for automotive applications and Ni-base superalloys for aerospace applications, involves both ordering and compositional clustering, and thus the characterization of the resulted precipitate microstructures requires both composition and order parameter fields. Another example is a composite microstructure of ferroelectric and ferromagnetic crystals, which requires two types of field variables, the electric polarization and magnetization.

In the phase-field method, the total free energy of an inhomogeneous microstructure is written as a functional of all the field variables that characterize the phase transitions and microstructures. In general, it contains four types of energetic contributions [6], i.e.,

$$F = \int_V \left[f_{\mathrm{local}} + f_{\mathrm{gra}} + f_{\mathrm{appl}}\right]\mathrm{d}V + \iint_{V,V'} \left[f_{\mathrm{nonlocal}}\right]\mathrm{d}V\mathrm{d}V', \quad (1)$$

where f_{local} is the local bulk chemical free energy density that is a function of one or more of the order parameters: c_i (composition of component i), η_i (long-range order parameters), p_i (polarization component i), m_i (magnetization component i), ε_{ij} (strain component ij), and ϕ_i (order parameters or fields describing the distribution of grains, dislocations, etc.). f_{gra} is the gradient energy density, i.e., the energy penalty for the inhomogeneity in the order parameter fields. It is non-zero only at and around interfaces, and, therefore, its introduction automatically includes the domain wall energy contribution. f_{appl} represents the coupling potential energy between applied fields such applied stress, electric field, or magnetic field and the corresponding order parameters like strain, polarization, and magnetization. The last term in Eq. (1) includes contributions from any one or more of the long-range interactions such as elastic, electrostatic, and magnetostatic interactions. It is the competition among the different contributions to the total free energy that is responsible for the formation of many fascinating microstructure patterns observed during various phase transformations and microstructure coarsening processes.

In phase-field models, the evolution of conserved fields, c_i, through diffusion obeys the Cahn–Hilliard equation [7], whereas the non-conserved fields, η_p (including polarization), are governed by the Allen–Cahn equation [8], i.e.,

$$\frac{\partial c_i(\mathbf{r},t)}{\partial t} = \nabla M_{ij} \nabla \frac{\delta F}{\delta c_j(\mathbf{r},t)}, \quad (2)$$

$$\frac{\partial \eta_p(\mathbf{r},t)}{\partial t} = -L_{pq} \frac{\delta F}{\delta \eta_q(\mathbf{r},t)}, \quad (3)$$

where M_{ij} and L_{pq} are related to atom or interface mobility. F is the total free energy of a system which is a functional of all the relevant conserved and non-conserved fields given by Eq. (1).

The evolution profiles of the field variables, and thus the microstructure evolution, are obtained by numerically solving the systems of evolution equations subject to appropriate initial and boundary conditions. Most of the phase-field simulations employ the second-order finite-difference discretization in space using uniform grids and the forward Euler method for time stepping to solve the phase-field equations for simplicity. It is well known that in such an explicit scheme, the time step has to be small to keep the numerical solutions stable. Dramatic savings in computation time and improvement in numerical accuracy can be achieved by using more advanced numerical approaches such as the semi-implicit Fourier spectral method [9]. Spectral discretization is particularly convenient and attractive for systems with long-range interactions. In addition, to effectively resolve the interfacial dynamics, particularly for a system involving very different characteristic spatial scales, e.g., very large domain sizes with very few interfaces, adaptive mesh schemes are desirable. This can, in principle, be achieved by working with both a computational space with uniform grids and a real space with adaptive grids. For complicated geometries of a computational domain, finite element methods may be more suitable.

To perform phase-field simulations of a given system, it requires the knowledge of structures and properties of individual structural features in a microstructure, which can be obtained by experiments or using atomistic level first-principles calculations. The input information required includes the bulk chemical free energy as a function of order parameters, the elastic constants, and the lattice parameter dependence as a function of order parameters for determining the elastic energy contribution to the thermodynamics of a microstructure. For ferroelectric and ferromagnetic crystals, the lattice parameter dependences on polarization and magnetization are described by the electrostrictive or magnetostrictive coefficients. The interfacial or domain wall energies together with the bulk free energy density are used to determine the gradient energy coefficients. For a number of special cases such as diffusional ordering and phase separation on a fixed crystalline lattice, it is possible to calculate the gradient energy coefficients using interatomic interaction energies. Furthermore, diffusional mobility of different atomic species involved in a microstructure evolution process as well as the mobility of an interface or a domain wall determines how fast the field variables and thus the microstructures evolve as a function of time.

The MGI for Global Competitive also states that “These computational tools are still not widely used due to industry’s limited confidence in accepting non-empirically based conclusions. Materials scientists have developed powerful computational tools to predict materials behavior, but these tools have fundamental deficiencies that limit their usefulness. The primary problem is that current predictive algorithms do not have the ability to model behavior and properties across multiple spatial and temporal scales;…” [1]. This is certainly also true for phase-field method. Although phase-field models have been developed for many different materials processes, they are not yet widely used in industry. To make phase-field method widely acceptable in industry, several new developments are required. The first is to develop multiscale models to predict microstructure evolution starting from first principles. There have been efforts to obtain all the necessary thermodynamic information for the input to a phase-field model from first-principles calculations combined with cluster expansions; it includes the bulk free energies, elastic constants, and lattice parameters of the matrix and precipitate phases, as well as the interfacial energy and its anisotropy [10]. For modeling the evolution of relatively complex microstructures, such information passing from one level to another seems to be the most realistic approach for multiscale modeling. There is also a need to combine the phase-field modeling of microstructure evolution and effective property calculation of a microstructure to obtain the temporal evolution of properties or to simply use the microstructure evolution obtained from a phase-field simulation in a constitutive model to predict the materials behavior, e.g., to use a strengthening model to predict the effect of precipitation on alloy strengthening. Linking microstructure evolution to property prediction is critically important for practical applications.

For applications to industrially relevant problems, it is also important to develop phase-field models for truly multicomponent alloys. In such cases, it is not possible to obtain all the necessary structural, thermodynamic, and kinetic parameters directly from first principles atomistic calculations. As a result, phase-field models are increasingly relying on existing or future thermodynamic, kinetic, and crystallographic databases obtained from empirical modeling. For example, it is possible to directly construct the free energy function of a phase-field model from existing databases using the calculation of phase diagram (CALPHAD) method [11–17]. The compositional dependence of atomic mobilities from databases can also be incorporated (see, for example, Refs. [16, 17]). However, in order to take into account the effect of elastic energy in solid-state processes, additional databases, such as the crystallographic lattice parameters and elastic constants, have to be constructed. Effort of constructing lattice parameter databases is already underway [18]. With independently assessed reliable databases, it will be possible to predict the microstructure evolution in complex multicomponent alloys using the phase-field method.

"…In addition, software tools that utilize the algorithms are typically written by academics for academic purposes in separate universities, and, therefore, lack user-friendly interfaces, documentation, robustness, and the capacity to scale to industrial-sized problems. These deficiencies inhibit efficient software maintenance and can result in software failures. Significant improvements in software and the accuracy of materials behavior models are needed." [1]. Indeed, many research-grade computer codes have been developed, mostly using the FORTRAN language. Typically, when a graduate student started to work a new problem, a new set of codes were developed. Although sometimes, one or two subroutines can be borrowed from a set of old codes with small modifications, most of the codes need to be rewritten for a new problem. Furthermore, when a student graduated, no one continues to maintain the specific set of codes. Furthermore, even a change of boundary conditions will require significant modifications of a code. Although it is a very good training for a graduate student to go through the whole programming process him or herself, there is a lot of time wasted in the process of writing codes for each specific problem. For example, in our own lab, we have many versions of phase-field codes for various materials problems, e.g., precipitate morphologies in Al–Cu alloys, Ni–Al alloys, Ni–Al–Mo alloys, grain growth, Ostwald ripening, spinodal phase separation, simultaneous grain growth and Ostwald ripening, ferroelectric domains in bulk and thin films, ferromagnetic domains, ferromagnetic shape memory alloys, etc. Therefore, after generating research-grade codes for more than a dozen years, we are in a process of redesigning and reengineering our existing phase-field codes to be modular, portable, and extensible.

In summary, phase-field method will be one of the main computational tools in the MGI for predicting mesoscale microstructure evolution and for linking the atomistic/electronic calculations to the macroscopic responses of heterogeneous materials. Major efforts are still required to develop phase-field models which can handle multicomponent systems at spatial and time scales compared to industrial materials processes, user-friendly/well-documented phase-field codes which are scalable and modular, and databases for the input to phase-field simulations.

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