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Phase transformations at interfaces: Observations from atomistic modeling

T. Frolov [a,*], M. Asta [b], Y. Mishin [c]

[a] Lawrence Livermore National Laboratory, Livermore, CA 94550, USA
[b] Department of Materials Science and Engineering, University of California, Berkeley, CA 94720, USA
[c] Department of Physics and Astronomy, MSN 3F3, George Mason University, Fairfax, VA 22030, USA

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ABSTRACT

We review the recent progress in theoretical understanding and atomistic computer simulations of phase transformations in materials interfaces, focusing on grain boundaries (GBs) in metallic systems. Recently developed simulation approaches enable the search and structural characterization of GB phases in single-component metals and binary alloys, calculation of thermodynamic properties of individual GB phases, and modeling of the effect of the GB phase transformations on GB kinetics. Atomistic simulations demonstrate that the GB transformations can be induced by varying the temperature, loading the GB with point defects, or varying the amount of solute segregation. The atomic-level understanding obtained from such simulations can provide input for further development of thermodynamics theories and continuous models of interface phase transformations while simultaneously serving as a testing ground for validation of theories and models. They can also help interpret and guide experimental work in this field.

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1. Introduction

Recent years have seen a rapid growth of evidence suggesting that materials interfaces are capable of first-order structural transformations in which the interface properties (such as solute segregation, excess volume, mobility or sliding resistance) undergo discontinuous changes [1]. Experiments have revealed a potentially important role of grain boundary (GB) phase transitions (sometimes referred to as "complexion transitions" [1,2]) in abnormal grain growth in ceramics [2], activated sintering [3] and liquid metal embrittlement [4]. Layering transitions associated with GB segregation were investigated using lattice gas models [5,6], first-principles calculations [7] as well as advanced electron microscopy and spectroscopy methods [8–10]. Experimental investigation of the potential impact of GB phase transitions on microstructure and other materials properties is currently a highly active area of research [1,4,11–13]. The experimental studies have raised a number of fundamental questions concerning the thermodynamic nature of the interface phases, their atomic structures and kinetic properties. A unified thermodynamic description of bulk and low-dimensional phases has been recently proposed [14], phase rules for phases of any dimensionality have been formulated, and adsorption equations for interface phases and line defects separating such phases have been derived [14]. Phase-field models have been developed [2,15,16], predicting a variety of possible interface transformations and mapping them onto bulk phase diagrams.

Although fundamentally important, the thermodynamic analysis [14,17–19] and phase-field models [2,15,16] do not provide atomic-level insights into interface phases and phase transformations. The goal of this paper is to review the recent progress in atomistic modeling of interface transformations, focusing on GBs in metallic systems as an important practical case. Although molecular dynamics (MD), Monte Carlo (MC) and other atomistic simulation methods have been successfully applied to study interfaces for a long time [20,21], it has not been until very recently that it became possible to identify and structurally characterize individual GB phases, compute their thermodynamic properties, and observe transformations among them. We describe the recent work on structural transformations in single-component GBs (Section 2), in binary alloys (Section 3), and the effect of such transformations on GB migration and short-circuit diffusivity (Section 5). In Section 5 we discuss existing challenges in this field and outline future work.

2. Grain boundary phase transitions in pure metals

2.1. The multiplicity of ground-state grain boundary structures

Atomistic computer simulations have proven to be an invaluable tool for the study of GB properties [21]. Such simulations have

* Corresponding author.

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been successfully applied to predict GB structures and calculate their thermodynamic and kinetic properties, such as GB free energies, diffusivities and mobilities as functions of temperature and chemical composition [21–30]. However, despite the extensive research, there has been no convincing simulation evidence of GB phase transformations until very recently (except for the dislocation-pairing transition in relatively low-angle GBs [31]). It has been demonstrated that the critical impediment to observations of such transformations was rooted in inadequate simulation methodology, namely, in fixing the total number of atoms and using periodic boundary conditions. In order to sample all possible atomic configurations, atoms need to be added to or removed from the GB region [32–36]. To overcome this shortcoming of the previous simulations, a new simulation methodology has been developed that allows for variations of the atomic density in the GB region as the latter approaches thermodynamic equilibrium [37]. Applications of this methodology have led to the discovery of multiple GB phases and phase transitions by varying the temperature and/or concentration of impurities or point defects [22,37,38].

The new simulation approach has been tested by studying the $\Sigma5(210)$ and $\Sigma5(310)$ symmetrical tilt GBs in several fcc metals modeled with embedded-atom method potentials. These are representative high-angle, high-energy boundaries that have been extensively investigated in the past. Their choice was additionally motivated by the recent experimental measurements of Ag radiotracer diffusion in Cu bicrystals with the $\Sigma5(310)$ GB [39], which revealed a peculiar temperature behavior of the GB diffusivity that suggested a possible structural transformation. To test this hypothesis, atomic structures of the two $\Sigma5$ GBs were optimized with respect to both atomic density and rigid translations of the grains [37]. It was found that at 0 K, the GB energy as a function of the GB density (measured as the fraction of atoms in (210) and (310) planes) exhibits several local minima representing different GB phases (Fig. 1(a)). In each boundary, one minimum corresponds to the long-known structure composed of kite-shape structural units obtained without addition or removal of atoms (Fig. 1(b and d)). Other minima are new and represent the filled-kite and split-kite GB structures (Fig. 1(c, e, f)). These structures are more complex and are either non-periodic or have a long period whose exact value remains unknown. These structures were obtained in simulation blocks with a large GB area and should be considered as approximants of the actual ground-state structures. It is possible that structures with even lower energies could be found in still larger simulation blocks. Remarkably, and contrary to the common belief, none of the tested interatomic potentials predicts the normal kite structure to be the lowest in energy for the $\Sigma5(210)$ GB.

It should be noted that the phases found in the $\Sigma5$ GBs are characterized by different excess properties, such as the excess volume and the interface stress [37]. These differences may result in long-range elastic strain fields around interface phase junctions in multi-phase states, which in turn can affect the coexistence of different GB phases and interact with dislocations and other elements of the microstructure.

2.2. Temperature-induced grain boundary transitions

Atomistic simulations have shown that GB phases can reversibly transform to each other with temperature [37]. Since such transformations require significant changes in atomic density in the GB region, the conventional simulation methodology with periodic boundary conditions and a fixed number of atoms cannot be applied. To enable automatic adjustment of the atomic density during the transformation, a different methodology has been proposed in which one or both edges of the GB terminates at an open surface (Fig. 2(a)). In this setup, provided the temperature is high enough, atoms can leave or enter the GB by diffusion to/from the surface. This effectively makes the GB an open thermodynamic system capable of exchanging atoms with a reservoir, a condition which naturally exists under experimental conditions.

As an example, Fig. 2(a) shows a Cu bicrystal with the $\Sigma5(310)$ boundary annealed at 800 K ($0.6T_m$, $T_m = 1327$ K being the melting temperature predicted by this potential) for tens of nanoseconds. The zoomed-in views reveal the original normal-kite GB structure on the left and a new, split-kite structure on the right. The latter nucleates at the surface and gradually propagates inside the bicrystal during the simulation. Its growth is enabled by the supply of extra atoms from the surface, a process which is kinetically controlled by GB diffusion. At a certain temperature, the two GB phases can coexist in thermodynamic equilibrium separated by a line defect representing a one-dimensional phase boundary between two two-dimensional phases. Knowledge of thermodynamic and topological properties of these unusual defects is important for the understanding of GB phase transitions (particularly, GB phase nucleation). These defects deserve a detailed study in the future. The observation of coexistence of GB phases with different densities separated by an atomic-width line defect confirms that the phase transformation is first order in character. Similar fully reversible temperature-induced phase transitions were found in the $\Sigma5(210)$ boundary [37].

2.3. Grain boundary transitions induced by point defects

During GB phase transformations, the boundary absorbs or rejects a large amount of atoms. This suggests that a phase transformation can be induced by injection or removal of a suitable number of point defects at a fixed temperature. This was indeed confirmed by simulations in which a GB phase was initially created in a periodic supercell isolated from external sources or sinks of atoms as in Fig. 3(a). A number of vacancies or interstitial atoms was then introduced into the GB region and the system was re-equilibrated by an MD run. For example, 80 interstitial atoms (the number required for transformation to the split-kite phase) were introduced into the normal-kite structure of the $\Sigma5(310)$ GB followed by an anneal at 800 K. A possible outcome could be a uniform redistribution of the extra atoms in the initial GB structure. Instead, a first-order transformation to the split-kite phase was observed as illustrated in Fig. 3(c). This transformation was fully reversible: when the same number of vacancies was subsequently introduced into the split-kite phase, the latter transformed back to normal kites (Fig. 3(e)). As a result of this phase transformation cycle, the boundary returned to its initial state having annihilated a large number of point defects. Analogous transformation cycles were observed upon loading of point defects into the $\Sigma5(210)$ GB.

These simulations suggest that interfacial phase transformations can greatly increase the capacity of GBs to absorb non-equilibrium point defects. This finding may have important practical implications for materials operating under extreme conditions. For example, the radiation tolerance of many nuclear materials depends on the efficiency of GBs as sinks of vacancies and interstitials created during irradiation by energetic particles [40–43]. GB phase transformations present a novel mechanism of radiation damage healing in such materials.

3. Segregation-induced grain boundary transitions

In technological applications, dopants and impurities can play a dominant role in microstructure evolution and properties. Recent experimental studies of doped ceramics revealed discontinuous