Segregation-induced phase transformations in grain boundaries

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Phase transformations in metallic grain boundaries (GBs) present significant fundamental interest in the context of thermodynamics of low-dimensional physical systems. We report on atomistic computer simulations of the Cu-Ag system that provide direct evidence that GB phase transformations in a single-component GB can continue to exist in a binary alloy. This gives rise to segregation-induced phase transformations with varying chemical composition at a fixed temperature. Furthermore, for such transformations we propose an approach to calculations of free-energy differences between different GB phases by thermodynamic integration along a segregation isotherm. This opens the possibility of developing quantitative thermodynamics of GB phases, their transformations to each other, and critical phenomena in the future.

Motivation. Recent years have seen a rising interest in phase transformations in two-dimensional systems such as grain boundaries (GBs) and other interfaces. Experimentally, a number of GB phases with discrete thickness (single layer, bilayer, etc.) have been found in binary and multicomponent metallic systems [1–3]. Different GB phases have also been observed in ceramic materials, where they are referred to as intergranular thin films or "complexions" [3–5]. Recently, a methodology has been developed for identification and structural characterization of GB phases in single-component metallic systems by atomistic computer simulations [6,7]. By applying this methodology, several different phases and reversible temperature-induced transformations between them were discovered in symmetrical tilt $\Sigma5(210)[001]$ and $\Sigma5(310)[001]$ GBs in face-centered cubic metals, Σ being the reciprocal density of coincidence sites, [001] the tilt axis, and (210) and (310) the GB planes. For the $\Sigma5(310)[001]$ GB in Cu, Ag GB diffusion coefficients computed separately for two GB phases [7] accurately reproduced the break in the temperature dependence of Ag GB diffusion coefficients measured experimentally by the radio-tracer method [8]. This agreement provided convincing experimental evidence for the existence of phase transformations in metallic GBs. Furthermore, such transformations have been shown to have a strong effect on shear-coupled GB motion and shear strength [9].

When studying Ag impurity diffusion in the Cu $\Sigma5(310)[001]$ GB [7], it was found that two GB phases stable at low and high temperatures displayed different segregation patterns, namely, a single layer and bilayer, respectively. However, the effect of segregation on the GB transformation temperature was not studied either in Ref. [7] or in any previous work. Furthermore, while the proposed methodology [6,7] enables direct observation of GB phase transformations by atomistic simulations, there have been no experimental or theoretical *quantitative* estimates of free-energy differences between different GB phases.

The goal of this paper is to report on atomistic simulations of a segregation-induced GB phase transformation in the Cu-Ag system, and to demonstrate an approach to calculations of free-energy differences between GB phases. Although we were able to detect segregation-induced transitions in both $\Sigma5$ GBs mentioned above, in this paper we focus the

attention on the $\Sigma5(210)[001]$ GB, which is different from the boundary studied earlier [7]. This choice was dictated by the higher transformation temperature in this boundary, permitting equilibration of its structure on relatively short time scales. However, the proposed approach can be readily extended to other GBs in the future.

Methodology. Our main simulation methods are molecular dynamics (MD) and semi-grand canonical Monte Carlo (MC) simulations with Cu-Ag interactions described by an embedded-atom potential [10]. The MD simulations utilized the LAMMPS code [11], while for the MC simulations we used the parallel MC algorithm developed by Sadigh *et al.* [12]. The latter alternates MC switches of atomic species (swaps) with MD runs implemented in LAMMPS. In this work, the fraction of swapped atoms was chosen to be 0.3 and the MD runs between the MC swaps comprised 1000 integration steps of 0.2 fs each. In the MC simulations, the temperature T and diffusion potential M of Ag relative to Cu are fixed while the distribution of Ag atoms over the system can vary to reach thermodynamic equilibrium. Typical simulation times were between 100 and 280 ns measured by the total number of MD steps. Images of the GB structures were produced with the visualization tool ATOMEYE [13].

Two types of simulation block were created. For finding the GB phase transformation point, the block contained a GB terminated at two free surfaces normal to the [120] direction z. In the x and y directions aligned with the [001] and [210] axes, respectively, the boundary conditions were periodic. (Due to the periodic condition in y, the block effectively contained two GBs.) The system contained 101 031 atoms and had the dimensions of $5.1 \times 16.5 \times 150$ nm^3. The open surfaces serve as sinks and sources of atoms that can penetrate in and out of the boundary to adjust its local atomic density to reach equilibrium. It has been previously shown [6] that this simulation setup permits observation of GB phase transformations in elemental systems. In this work, this simulation approach is extended to segregation-induced phase transformations in binary systems.

For computing the amount of GB segregation, two smaller blocks were created by carving rectangular regions out of the larger system. Each of the smaller blocks contained a single GB phase and had periodic boundary conditions in all three

directions. The numbers of atoms in the blocks containing the split kite and filled kite phases were, respectively, 33 677 and 33 576. Because this construction isolated the GB phases from sinks and sources of atoms, the GB was unable to vary its local density and thus maintained its phase during the subsequent simulations. This enabled us to study thermodynamic properties of the two phases individually over a range of compositions.

Results. During the Monte Carlo simulations with open surfaces at given T and M, it was found that after a long run the GB always reaches equilibrium with a structure of one of the two phases. The two phases exhibit different segregation patterns: while in the filled kite phase the Ag atoms segregate to the GB plane as a single (but not complete) layer, in the split-kite structure they form a bilayer. The two segregation patterns are illustrated in Fig. 1.

When M changes at a fixed temperature, the GB either reequilibrates to a new state of the same phase or transforms to another phase. As an example, Fig. 2 illustrates a phase transformation at the temperature of 900 K. The initial state of the boundary is split kites created by a previous MD run. The diffusion potential is then switched to $M = 0.48$ eV and a new run is started. During this run, the filled kite phase nucleates at the GB/surface junction and begins to grow into the boundary, converting its structure to filled kites. The boundary between the two GB phases is a line defect that can be considered to be a two-dimensional analog of interphase boundaries in bulk thermodynamics. This two-dimensional interphase boundary penetrates into the GB, and after a 100-ns-long simulation
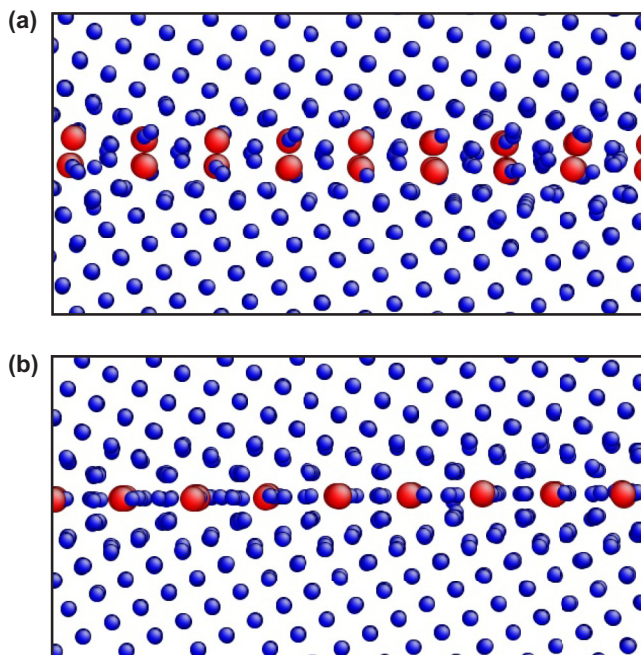

(a)

(b)

FIG. 1. (Color online) Ag GB segregation patterns in the (a) split-kite phase and (b) filled-kite phase of the Cu Σ5(210)[001]. The tilt axis [001] is normal to the page. The smaller blue and larger red spheres represent Cu and Ag atoms, respectively. The segregation formed at the temperature of $T = 900$ K and diffusion potential $M = 0.9$ eV. The images are shown after a short MD run at $T = 10$ K to remove thermal noise.
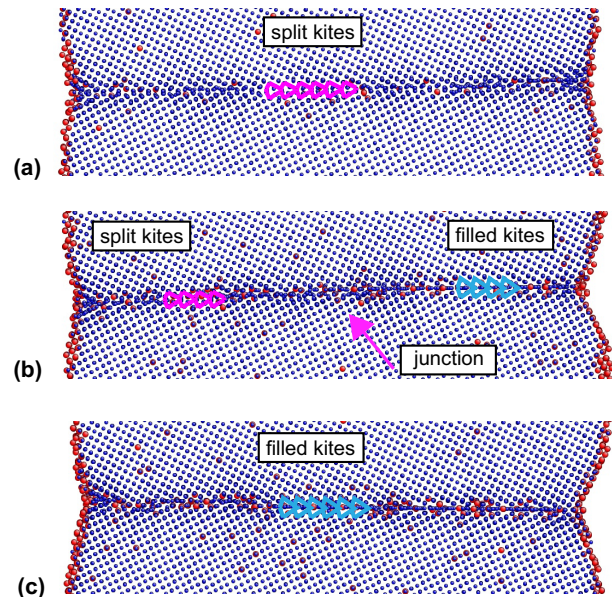

FIG. 2. (Color online) GB phase transformation at $T = 900$ K and $M = 0.48$ eV. (a) Initially the GB is in the split-kite phase. (b) Nucleation of the filled-kite phase at the surface. (c) The GB has completely transformed to the filled-kite phase.

reaches the opposing surface, converting the entire boundary into the filled kite phase.

To find the equilibrium state between the two GB phases, simulations were performed for a set of diffusion potentials starting with a GB containing both phases [e.g., Fig. 2(b)]. It was determined that in all simulations with $M > M^* = 0.33$ eV, the interphase boundary moved in one direction and the GB ended up in the split-kite phase. In simulations with $M < M^*$, the interphase boundary moved in the opposite direction, converting the GB to the filled kite phase. It was thus concluded that, at this particular temperature, the two GB phases coexist at $M = M^*$. In simulations with exactly this value of the diffusion potential, both GB structures continued to coexist during a 280-ns-long simulation run, the longest that we could afford with available computational resources. The obtained equilibrium value of M corresponds to the grain composition of $c = 0.02$ at. %Ag. Since the two phases are in equilibrium at this composition, their GB free energies are equal:

$$\gamma^{\mathrm{SK}} = \gamma^{\mathrm{FK}} \equiv \gamma_*. \qquad (1)$$

GB segregation in individual GB phases was computed in periodic simulation blocks containing a single phase. As in previous work [14], the amount of segregation was defined as the excess number N_{Ag} of Ag atoms per unit GB area relative to a perfect lattice region with the same composition as the grains and containing the same total number N of atoms as the bicrystal. This type of segregation is denoted $[N_{\mathrm{Ag}}]_N$ and measured in Å^{-2}. It was computed by averaging over 250 snapshots saved after every ten MC swaps.

Figure 3 presents the segregation isotherms computed for individual phases at 900 K. Each curve stops at a point where the GB structure becomes too disordered to identify it unambiguously with a particular phase. Note that segregation in the
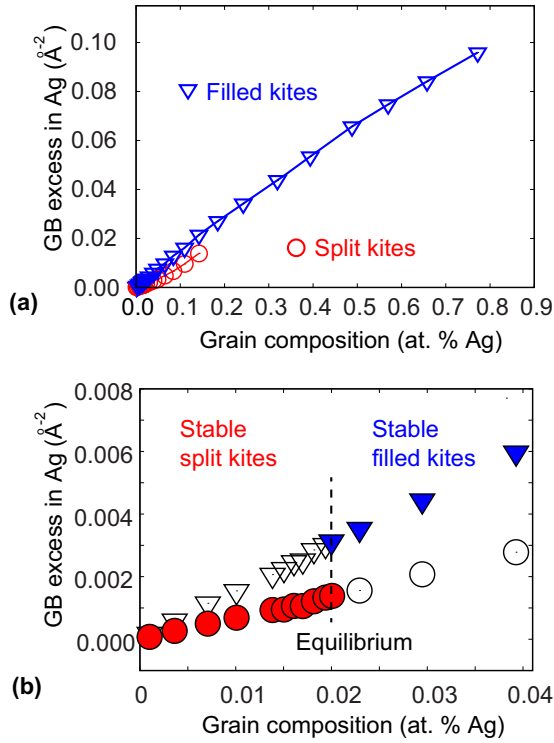
FIG. 3. (Color online) Ag GB segregation isotherms for the split-kite (circles) and filled-kite (triangle) phases at the temperature of 900 K. The GB excess of Ag atoms per unit area is plotted as a function of Ag concentration in the grains. (a) Summary of all results. The curves end when the GB phase undergoes a disordering transition. (b) Zoomed view of the composition range near the GB phase transformation at $c = 0.02$ at. % Ag. The filled and open symbols represent data for the stable and metastable states, respectively.

filled kite phase is systematically higher than in the split-kite phase, even though the former exhibits a bilayer segregation while the latter a single-layer segregation. Thus, caution should be exercised in the interpretation of experimental images of segregated GBs: a bilayer segregation pattern is not necessarily an indication of stronger segregation. In the zoomed view of this plot displayed in Fig. 3(b), the filled circles represent grain compositions for which the GB transformed to split kites. Likewise, the filled triangles represent grain compositions for which the GB transformed to filled kites. The composition of $c = 0.02$ at. % Ag marked by the dashed line separates the intervals of thermodynamic stability of the two phases and is identified with the point of GB phase coexistence. At this point, the amount of segregation jumps discontinuously from $[N_{Ag}]_N = 0.0014 \text{ Å}^{-2}$ to $[N_{Ag}]_N = 0.0031 \text{ Å}^{-2}$.

The obtained isotherms (Fig. 3) contain all information needed for calculations of free energies of the GB phases at this temperature. Indeed, for each phase, the GB free energy γ follows the adsorption equation [14]

$$d\gamma = -[S]_N dT - [N_{Ag}]_N dM + \sum_{i,j=1,2} (\tau_{ij} - \gamma) de_{ij}, \quad (2)$$

where $[S]_N$ is the excess entropy defined in the same way as the segregation, τ_{ij} is the GB stress, and e_{ij} is the lateral strain tensor parallel to the GB plane. Equation (2) is a particular

case of a more general adsorption equation derived in the previous work [14]. For the present case, this equation has been simplified due to the absence of applied mechanical stresses. Furthermore, given the narrow composition interval around the phase transformation, the lateral strain is extremely small and the last term in Eq. (2) can be neglected. As a result, Eq. (2) can be integrated with respect to M at a fixed temperature to obtain the free energy of each GB phase relative to their common value γ_*:

$$\gamma - \gamma_* = -\int_{M_*}^{M} [N_{Ag}]_N dM. \quad (3)$$

This free energy is a function of M but can be readily converted to a function of c.

The function $M(c)$ is known from MC simulations of the perfect lattice. To perform the integration, this function was fitted by the expression $M(c) = a_0 + a_1 c + a_2 c^2 + a_3 \ln(c)$ with adjustable coefficients a_i. Likewise, the segregation isotherms (Fig. 3) were fitted by $[N_{Ag}]_N(c) = b_1 c + b_2 c^2$ with adjustable coefficients b_i for each phase. After this, the integration was executed analytically on either side of the equilibrium point, including extrapolation to pure Cu ($c = 0$). The obtained GB free energies, $\gamma^{SK} - \gamma_*$ and $\gamma^{FK} - \gamma_*$, are plotted in Fig. 4(a) as functions of grain composition. The striking observation is that the free-energy difference between the two phases is very small. Even in the pure Cu limit, this difference is as small as 2.2 mJ/m^2 (compare with
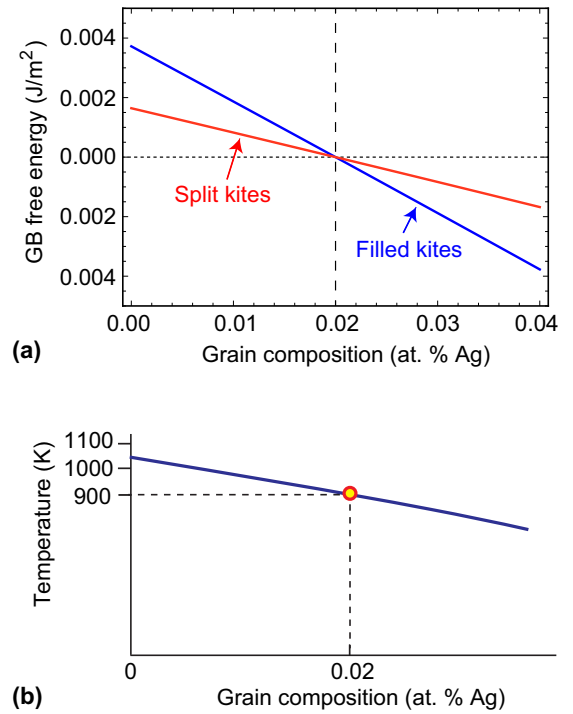

FIG. 4. (Color online) (a) Free energies of two GB phases, γ^{SK} and γ^{FK}, relative to their coexistence value γ_* as functions of Ag concentration in the grains. The phase transformation occurs at $c = 0.02$ at. % Ag. The results were obtained by thermodynamic integration at 900 K. (b) Schematic phase diagram of GB phase transformations with the open circle showing the result of this work.

the 0 K energy of this boundary, 0.951 J/m^2) [6]. Near the phase equilibrium point ($c = 0.02$ at. % Ag), the phase transformation can still be reliably detected when $\gamma^{\text{SK}} - \gamma^{\text{FK}}$ is less than 0.1 mJ/m^2. These numbers demonstrate that, using the proposed simulation methods, thermodynamic properties of GB phases can be characterized with a high precision, including accurate location of phase transformation points.

For pure Cu, the energy difference between the two GB phases at 0 K is $\gamma^{\text{FK}} - \gamma^{\text{SK}} = 17$ mJ/m^2 [6]. The respective free energy difference at 900 K is 2.2 mJ/m^2, i.e., a factor of 7 less. This is consistent with the proximity of temperature-induced phase transformation in this GB, which was previously found to occur around 1050 K [6].

Conclusions. We have demonstrated that the temperature-induced GB phase transformations found in previous work [6] continue to exist in the presence of segregating solute atoms, giving rise to segregation-induced GB phase transformations. Such transformations are accompanied by a discontinuous jump in the amount of segregation and a change in the segregation pattern from a single layer to a bilayer. We have studied this transformation at a single temperature of 900 K. However, considering the small solute concentration causing this transformation, it is likely to be a point on a phase transformation line that can be conveniently shown in temperature-composition coordinates [Fig. 4(b)]. This line terminates at the temperature axis at around $T = 1050$ K. Another segregation-induced structural transformation was previously found in a twist GB in the Ni-Pt system [15]. However, by contrast to the present work, there was no evidence that a similar transformation occurs in the pure Ni boundary. Most likely, that transformation represents an isolated region on the temperature-composition phase diagram that is not connected to the temperature axis. These two cases suggests that future atomistic simulations may reveal a rich variety of congruent [16] GB phase transformations, which can be presented as T-c phase diagrams by analogy with bulk systems.

The thermodynamic integration scheme proposed in this work enables free-energy calculations for individual GB phases (relative to their common value at equilibrium) and construction of GB phase diagrams. In particular, the entire phase transformation line shown schematically in Fig. 3(b) can be calculated by the same method. This line could be tested against predictions of interface thermodynamics. Because Eq. (1) must remain valid along this line, we can use the adsorption equation (2) for each phase to derive the following equation for the slope of the equilibrium line:

$$\frac{dT}{dc} = -\frac{\Delta[N_{\text{Ag}}]_N (\partial M / \partial c)_T T}{\Delta[U]_N - M\Delta[N_{\text{Ag}}]_N + \Delta[N_{\text{Ag}}]_N (\partial M / \partial T)_c T},$$

(4)

where $[U]_N$ is the excess internal energy of the GB and the symbol Δ denotes differences between properties of the two phases. The quantities appearing in the right-hand side can be computed separately to compare the right-hand side with the actual slope of the line.

The proposed method can be applied for calculations of not only phase equilibrium lines but also spinodal lines and critical points. For example, the obtained segregation isotherms [Fig. 3(a)] terminate at points of GB disorder. While investigation of the nature of this disordering transition is beyond the scope of this paper, it is possible that these points signify transformations to new phases that are yet to be discovered. Investigation of critical phenomena in two-dimensional GB phases may present significant fundamental interest.

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