Abstract

Computing the grain boundary (GB) counterparts to bulk phase diagrams represents an emerging research direction with potentially broad impacts. Using a classical embrittlement model system Ga-doped Al, this study demonstrates the feasibility of computing temperature- and composition-dependent GB diagrams to represent not only equilibrium thermodynamic and structural characters, but also mechanical properties. Specifically, hybrid Monte Carlo and molecular dynamics (MC/MD) simulations are used to obtain the equilibrium GB structure as a function of temperature and composition. Simulated GB structures are validated by aberration-corrected scanning transmission electron microscopy. Subsequently, MD tensile tests are performed on the simulated equilibrium GB structures. GB diagrams are computed for not only GB adsorption and disorder, but also interfacial structural and chemical widths, MD ultimate strength, and tensile toughness. A model is established to forecast the ductile-to-brittle transition. This study establishes a new paradigm to compute a spectrum of GB diagrams to enable the investigation of the unique GB composition-structure-property relationship.
Introduction

In polycrystalline materials, grain boundaries (GBs) are the ubiquitous crystal imperfection that can often control materials fabrication processing and performance.\textsuperscript{1-6} It has been long recognized that GBs can be treated as two-dimensional (2D) interfacial phases,\textsuperscript{7} which are more recently termed as “complexions” to differentiate them from thin GB precipitation layers of bulk (3D) phases.\textsuperscript{1,2,8-10} Recently, it was proposed to develop the GB counterparts to bulk phase diagrams as a generally useful materials science tool.\textsuperscript{11} Several types of GB diagrams have been computed via thermodynamic models,\textsuperscript{11-19} density functional calculations,\textsuperscript{20} atomistic simulations,\textsuperscript{21-23} and machine learning\textsuperscript{21}. To date, GB diagrams have only been developed to represent a limited number of thermodynamic and structural properties, mostly notably adsorption (\textit{i.e.}, the GB excess of solutes)\textsuperscript{18,21-24} and interfacial disorder\textsuperscript{11,14-17,21-24}. This work strives for further constructing GB diagrams to represent not only other useful equilibrium structural characters (\textit{e.g.}, GB structural and chemical widths) but also computed mechanical properties. Specifically, this study aims at using a classical model embrittlement system, Ga-doped Al, to establish an exemplar for a potential new paradigm.

Solute or impurity segregation (\textit{a.k.a.} adsorption in interfacial thermodynamics) at GBs can substantially alter their structural characters to influence various mechanical and other functional properties.\textsuperscript{1,3,5,25-31} Specifically, GB embrittlement (GBE) induced by segregation is one of the most classical phenomena in the physical metallurgy.\textsuperscript{4,26,28-34} While the Rice-Wang model offers a general thermodynamic framework,\textsuperscript{31} the atomistic mechanisms underpinning GBE are not fully understood, defying the scrutiny over a century. Liquid metal embrittlement (LME), where normally ductile metals can fail catastrophically in contact with certain liquid metals, represents a particular mystery in materials science.\textsuperscript{35-37} While there are other contributing factors, LME often occurs along with severe GBE. Here, Ni-Bi\textsuperscript{28} and Al-Ga\textsuperscript{32,34,38-41} represent two classical GBE and LME systems.

Moreover, the majority of prior atomistic studies focused on symmetric tilt or twist GBs that are relatively easy to image and model. The atomic-level embrittlement mechanisms of general GBs (\textit{a.k.a.} asymmetric GBs that are often of mixed tilt and twist characters) are poorly understood. However, the asymmetric and general GBs are ubiquitous and can often be the weaker link mechanically and chemically in polycrystalline materials that limits the performance. Recent
studies of two classical GBE systems, Bi vs. S doped Ni, revealed different characteristic interfacial structures that underpin the embrittlement of general GBs. In Ni-Bi, ordered bilayer adsorption of Bi caused LME,\(^{28}\) where each of the adsorbed layers can undergo reconstruction to form highly ordered interfacial superstructures.\(^{28}\) In Ni-S, more disordered bilayer-like and amorphous-like complexes with bipolar structural features have been discovered.\(^{26}\) However, the lacking of fast and reliable interatomic potentials in these systems prevent us from computing realistic GB diagrams via large-scale atomistic simulations. Al-Ga represent another classical GBE and LME system that exhibits somewhat different thermodynamic characters (e.g., Ga has substantial solid solubility in Al vs. limited solid solubilities of Bi or S in Ni) and interfacial structures.\(^{32-34,38-41}\) A fast and reliable embedded-atom model (EAM) potential has been developed and tested for Al-Ga,\(^{34,40,42}\) which enables us to use Al-Ga as our model system to compute GB diagrams to establish an exemplar. We should note that the bulk liquid Ga can also wet and penetrate to Al GBs to contribute to LME.\(^{38,41,43}\) The current study, however, focuses on the (undersaturated) single bulk solid solution phase region where severe GBE occurs (before the appearance of bulk Ga-based liquid metal).

Using a general GB in Al-Ga as the model system, we simulated equilibrium GB structure as a function of temperature and bulk Ga fraction. Subsequently, we conducted molecular dynamics (MD) tensile tests to study the mechanical response of the equilibrium GB structure with external loading. Consequently, we construct GB diagrams for not only Ga adsorption and interfacial disorder (that have been computed only for a limited number of three other systems\(^{21-23}\)) but also interfacial structural and chemical widths and computed mechanical properties (for the first time). This study greatly expands our capability to compute GB diagrams via atomistic simulations.

**Validation and Prelude: Trilayer-like Segregation in a Symmetric Tilt GB**

We adopted isobaric semi-grand canonical (constant \(N(\Delta \mu)PT\)) ensemble hybrid Monte Carlo and molecular dynamics (MC/MD) simulations to obtain equilibrium GB structures in Ga-doped Al using an EAM potential originally developed by the Srolovitz group.\(^{42}\) The EAM potential can reproduce Al-Ga binary phase diagram in agreement with experiments (as shown in Fig. S1 in the Supplementary Information). See Methods for the detailed computation procedure.

To validate our simulation methods and the EAM potential, we first model the trilayer-like segregation structure at a symmetric tilt \(\Sigma 11\) GB reported by Sigle \textit{et al.} (Fig. 1a).\(^{33}\) This largely
ordered trilayer-like structure also serves as a good (relatively simple) starting example to investigate Ga segregation at Al GBs. Here, we constructed this Σ11 (113)//(113) GB structure in a unit cell with 18480 atoms to perform hybrid MC/MD simulations. Subsequently, we simulated the scanning transmission electron microscopy (STEM) image based on the simulated GB structure (Fig. 1c). The simulated STEM image (Fig. 1b) clearly shows a trilayer-like structure, in a good agreement with experimental STEM image (Fig. 1a). Furthermore, both the line-by-line intensity profile (the cyan line in Fig. 1b) and the 2D averaged Ga atomic fraction profile across the GB (Fig. 1f) show a triple peaks pattern at the GB, consistent with the experimental observation.

In addition, we calculated disorder parameter ($\eta_{\text{Dis}}$) from the simulated GB structure for each atom following a procedure proposed by Chua et al. (where $\eta_{\text{Dis}} = 0$ for a perfect crystal and $\eta_{\text{Dis}} = 1$ for a liquid).44 A corresponding color map of $\eta_{\text{Dis}}$ is shown in Fig. 1d and the 2D averaged $\eta_{\text{Dis}}$ profile is shown in Fig. 1g. The GB core has a maximal $\eta_{\text{Dis}}$ value of ~0.5, which suggests the structure of this symmetric tilt GB to be relatively ordered (in comparison with the asymmetric and general GB shown in Fig. 2 and discussed in the next section). Moreover, we calculated centrosymmetry parameters (CSP) to measure the local lattice disorder using the OVITO code (where CSP = 0 represents the ideal crystal and positive CSP values indicates defects; see Methods).45,46 The CSP map (Fig. 1e) and the 2D averaged CSP profile (Fig. 1h) again confirmed the relatively ordered segregation structure at this symmetric tilt GB with a small maximal CSP value of ~7 (vs. ~18 for the asymmetric and general GB shown in Fig. 2). In summary, our hybrid MC/MD simulations can reproduce the trilayer-like Ga segregation structure in the Al Σ11 symmetric tilt GB that was previously observed in a bicrystal experiment.33 We have further revealed structural details of this (relatively simple and ordered) symmetric tilt GB.

**Segregation in an Asymmetric General GB**

Next, we investigated more complex and disordered segregation structures at asymmetric and general GBs. The detailed procedure for our polycrystal experiment was described in the Methods section. Fig. 2a shows an aberration-corrected (AC) STEM high-angle annular dark-field (HAADF) image of a representative asymmetric and general GB randomly selected from a Ga-doped Al polycrystalline specimen, where the orientation of the low-index grain surface is (110). The high brightness at the GB region suggests strong Ga segregation (Fig. 2a), which is evident quantitatively in the intensity profile (the yellow line in Fig. 2a). Moreover, the intensity profile
shows partial order in the GB region (indicated by arrows in Fig. 2a). The partially ordered Ga segregation structure can be further analyzed and demonstrated by performing line-by-line fast Fourier transformation (FFT) analysis of the STEM image, which is shown in the right panel of Fig. 2a.

To mimic this experimentally observed general GB shown in Fig. 2a, we selected an asymmetric Σ81 (110)/(787) GB of mixed tilt and twist characters for simulations. Here, one grain has the (110) terminal surface matching the general GB randomly selected in a polycrystal shown in Fig. 2a. The orientation of the other grain was selected to maintain a required periodic boundray condition while having a large Σ value of 81 to best represent a general GB. Subsequently, we performed hybrid MC/MD simulation at 300 K and $\Delta \mu = -0.4415$ eV (selected so that the simulated interfacial width matched the experimental observation, which corresponds to $X \approx 0.28X_{\text{Max}}$). The hybrid MC/MD simulated GB structure was shown in Fig. 2c, which clearly shows strong Ga segregation at the GB region. Based on this simulated GB structure, we further performed STEM image simulation (Fig. 2b). The simulated STEM image agrees well with experimental STEM image (Fig. 2b vs. 2a). The intensity peak and FFT analysis again confirm the partially ordered Ga segregation structure, which becomes more disordered at the GB core (the most middle region between the two abutting grains). To better quantify the disorder, we calculated the $\eta_{\text{Dis}}$ parameter from the simulated GB structure. The color map of the $\eta_{\text{Dis}}$ parameter (Fig. 2d) shows that the GB core are highly disordered with a $\eta_{\text{Dis}}$ value of ~1 (liquid-like), but Ga atoms close to bulk phases are more ordered with smaller $\eta_{\text{Dis}}$. The 2D averaged disorder profile $\eta_{\text{Dis}}(z)$ is shown in Fig. 2g. In addition, the GB core region has a large maximal CSP value of ~18 (Fig. 2h), which is $\approx 2.5$ times higher than that in the ordered (trilayer-like) symmetric tilt Σ11 GB (Fig. 1h). The combination of the $\eta_{\text{Dis}}$ and CSP profiles, along with the experimental and simulated STEM images, clearly confirms the (more) disordered Ga structure at the asymmetric Σ81 GB.

By calculating the full widths at half maximum (FWHMs) of the Ga composition $X_{\text{Ga}}(z)$ and $\eta_{\text{Dis}}(z)$ profiles, we found that the GB structural width ($\delta_{\text{GB}}^{\text{Structural}}$) calculated from the $\eta_{\text{Dis}}(z)$ profile is ~0.70 nm, which is smaller than the GB chemical width ($\delta_{\text{GB}}^{\text{Chemical}}$) of ~0.80 nm calculated from the $X_{\text{Ga}}(z)$ profile. This suggests that the Ga atoms near bulk regions are more ordered than those in the disordered GB core region at this low temperature (300 K).

In summary, our hybrid MC/MD simulations can reproduce not only the ordered trilayer-like
segregation structure in the (special) symmetric tilt GB but also more disordered segregation structure in more general and asymmetric GB observed in experiments. Therefore, our hybrid MC/MD simulations are validated. Since our primary interest is on the general GBs that are the weak link for mechanical and chemical degradation, we will use the asymmetric \( \Sigma 81 \) GB to represent general GBs to compute GB diagrams of both thermodynamic and mechanical properties in the subsequent in-depth investigation.

**GB Diagrams of Thermodynamic and Structural Properties**

To compute GB diagrams, we performed a series of isobaric semi-grand canonical ensemble hybrid MC/MD simulations to compute the equilibrium GB structure as a function of temperature \( (T) \) and chemical potential difference \( (\Delta \mu) \). See Methods for details of the simulations. Via hybrid MC/MD simulations of the bulk phases (grains), we also established a relation between \( \Delta \mu \) and the bulk Ga fraction \( (X = X_{Ga}) \) at each temperature. Subsequently, we can compute various GB properties (based on the simulated equilibrium GB structures) and plot the properties as functions of normalized temperature \( (T/T_m, \text{where } T_M \text{ is the melting temperature of Al}) \) and normalized bulk Ga fraction \( (X/X_{Max}, \text{where } X_{Max} \text{ is the maximal solid solubility of Ga in Al}) \) to construct GB diagrams.

We first computed two basic thermodynamic properties, GB adsorption \( (i.e., \text{the GB excess of Ga, } \Gamma_{Ga}) \) and GB excess of disorder \( (\Gamma_{Disorder}) \), as functions of \( T/T_M \) and \( X/X_{Max} \), via the following procedures. The GB excess of Ga can be determined by:

\[
\Gamma_{Ga} = \int_{-\infty}^{+\infty} [X_{Ga}(z) - X_{Ga}(\pm \infty)] dz,
\]

where \( X_{Ga}(z) \) is the 2D averaged Ga fraction profile (see, e.g., Fig. 2f) and \( X_{Ga}(\pm \infty) \equiv X \) is the bulk Ga fraction. The GB excess of disorder can be computed via:

\[
\Gamma_{Disorder} = \int_{-\infty}^{+\infty} [\eta_{Dis.}(z) - \eta_{Dis}(\pm \infty)] dz,
\]

where \( \eta_{Dis.}(z) \) is the 2D averaged disorder parameter profile (see, e.g., Fig. 2g) and \( \eta_{Dis}(\pm \infty) \approx 0 \) inside a crystalline grain \( (\eta_{Dis} = 0 \text{ for a perfect crystal at 0 K}) \). The computed GB adsorption and disorder diagrams are plotted in Fig. 3a and Fig. 3b, respectively.

Fig. 3a shows that the GB adsorption is high at low temperatures, which increases with increasing bulk Ga fraction. The corresponding \( \Gamma_{Ga} \text{ vs. } X/X_{Max} \) curves at different temperatures plotted in Fig. 3c show continuous changes without a first-order adsorption transition (resulted from an attractive Al-Ga pair-interaction as illustrated by a phenomenological model discussed subsequently). The computed GB disorder diagram (Fig. 3b), as well as the corresponding
\(I_{\text{Disorder}}\) vs. \(X/X_{\text{Max}}\) curves (Fig. 3d), shows that \(I_{\text{Disorder}}\) increases with increasing temperature and bulk Ga fraction. Fig. 3b also suggests that Ga addition can induce more disorder than temperature near the upper segment of the bulk solidus line (for \(T > \sim 0.4T_m\)).

Such GB adsorption and disorder diagrams have been constructed (only) for three other systems, Mo-Ni,\(^{22}\) Si-Au,\(^{23}\) and Cu-Ag,\(^{21}\) in prior studies (and only for the last case of Cu-Ag for asymmetric and general GBs in a most recent study\(^{21}\)). Here, Al-Ga represents the fourth system, yet the first GBE/LME system for a general GB, for which GB adsorption and disorder diagrams have been constructed via atomistic simulations. In comparison with the symmetric \(\Sigma 5\) tilt GB in Mo-Ni reported in a prior study,\(^{22}\) there is much less coupling between the GB adsorption and disorder in Fig. 3a vs. 3b for this asymmetric \(\Sigma 81\) mixed GB in Al-Ga. To establish and understand the GB composition-structure-property relationship, here we have taken a step forward to further compute GB diagrams to represent other GB equilibrium structural characters, as well as simulated mechanical properties in the next section, for the first time to our knowledge.

Specifically, the effective GB chemical and structural widths (\(\delta_{\text{GB}}^{\text{Chemical}}\) and \(\delta_{\text{GB}}^{\text{Structural}}\)) were calculated based on full widths at half maximum or FWHMs of the 2D averaged composition and disorder profiles; see, e.g., Fig. 2f for a representative \(X_{\text{Ga}}(z)\) and Fig. 2g for a representative \(\eta_{\text{Dis}}(z)\). On the one hand, the computed GB structural width diagram (Fig. 3f) shows similar characters as the computed GB disorder diagram (Fig. 3b), but with a narrower region of increased \(\delta_{\text{GB}}^{\text{Structural}}\) width near the upper half of the bulk solidus line (above \(-0.5T_m\)). On the other hand, the computed GB chemical width diagram (Fig. 3f) shows different characters from both GB adsorption diagram and the GB structural width diagram.

To further understand the \(T\)- and \(X\)-dependent GB complexion in the Al-Ga system, we further plot a GB diagram to represent the difference between \(\delta_{\text{GB}}^{\text{Structural}}\) and \(\delta_{\text{GB}}^{\text{Chemical}}\) in Fig. 3g. It is evident in Fig. 3g that \(\delta_{\text{GB}}^{\text{Structural}}\) is always larger than \(\delta_{\text{GB}}^{\text{Chemical}}\) at higher temperatures (\(T > 0.5T_m\)), and it becomes smaller than \(\delta_{\text{GB}}^{\text{Chemical}}\) at relatively low temperatures (but only) with moderate to high Ga adsorption. In Fig. 3g, the region where \(\delta_{\text{GB}}^{\text{Chemical}} > \delta_{\text{GB}}^{\text{Structural}}\) represents more ordered GB segregation structures (see, e.g., Fig. 2). In this region, the segregated Ga atoms are more ordered near the two abutting grains (for \(\frac{1}{2}\delta_{\text{GB}}^{\text{Chemical}} > |z| > \frac{1}{2}\delta_{\text{GB}}^{\text{Structural}}\)) but become more disordered at the GB core (for \(|z| < \frac{1}{2}\delta_{\text{GB}}^{\text{Structural}}\)). In contrast, the region where \(\delta_{\text{GB}}^{\text{Structural}} >\)
\(\delta_{\text{GB}}^{\text{Chemical}}\) represents more disordered GB complexions.

The widening of effective interfacial structural and chemical thickness (\(\delta_{\text{GB}}^{\text{Chemical}}\) and \(\delta_{\text{GB}}^{\text{Structural}}\)) near (but below) the bulk solidus line can have significant implications in the fast (invasive) Ga penetration at GBs in LME. The computed GB width diagrams shown in Figs. 3e-g suggest such interfacial widening is primarily promoted by Ga adsorption (analogues to a case of prewetting\(^{47}\)) at \(T < \sim 0.5\ T_m\), but by interfacial disordering (akin to premelting\(^{48}\)) at \(T > \sim 0.5\ T_m\). Overall, the GB complexion\(^1 (a.k.a.\ 2D\ interfacial\ phase)\) formed in Al-Ga can be considered as coupled GB prewetting and premelting,\(^5\) where the transition between the two regions are gradual (Fig. 3g). Thus, these new types of GB structural and chemical width diagrams (Figs. 3e-g) can provide additional structural details of the GB complexion, supplementing the GB adsorption and disorder diagrams that (only) represent the GB excess quantities.

**GB Diagrams of Simulated Mechanical Properties**

To understand the mechanical properties of the GBs, we performed MD tensile tests on the equilibrium GB structures obtained by hybrid MC/MD simulations. Representative stress (\(\sigma\)) vs. strain (\(\epsilon\)) curves for the MD tensile tests for a series of GBs equilibrated at different \(\Delta\mu\’s\) are shown in Supplementary Fig. S3. The maximal tensile stress in the MD simulation is denoted as the MD ultimate strength (\(\sigma_{\text{UTS}}^{\text{MD}}\)). In addition, the MD tensile toughness is defined as the integral of the stress: \(U_T^{\text{MD}} = \int_0^{0.2} \sigma(\epsilon)d\epsilon\). The details of the simulation and analysis procedures are described in Methods. Subsequently, we computed \(\sigma_{\text{UTS}}^{\text{MD}}\) and \(U_T^{\text{MD}}\) as functions of temperature and bulk composition to construct GB diagrams of mechanical properties, which are plotted in Fig. 4a and Fig. 4b. It is important to note the MD tensile tests were conducted at a high strain rate of \(\sim 5.4 \times 10^8 \text{ s}^{-1}\) due to the limitation of MD simulations. Thus, the absolute values of the MD simulated strength and tensile toughness cannot be directly compared with realistic experimental values, but the relative trends in the GB diagrams of MD mechanical properties can be useful.

Fig. 4a (the GB MD strength diagram) shows that the strength can be reduced by increasing either the bulk Ga fraction or temperature. The detrimental effects of Ga on \(\sigma_{\text{UTS}}^{\text{MD}}\) are more severe at low temperatures. In the intermediate temperature region (\(\sim 0.5\text{-}0.6 T_M\)), a high level of Ga can be tolerated in grains (but with little Ga segregation at GBs according to Fig. 3a). The high-strength region has a half-balloon shape in Fig. 4a. Fig. 4c further shows the \(\sigma_{\text{UTS}}^{\text{MD}}\ vs. X/X_{\text{Max}}\) curves at
different temperatures. For example, the computed $\sigma_{\text{UTS}}^{\text{MD}}$ is ~2.95 GPa at 300 K for “clean” GB (with little Ga adsorption) and it is reduced to ~ 1.06 GPa when $X/X_{\text{Max}}$ is ~0.70 (near the solubility limit at 300 K). By increasing the temperature, the computed $\sigma_{\text{UTS}}$ of the “clean” GB can also be reduced to ~1.03 GPa at ~0.93$T_m$ due to the high-temperature reduction of the strength. Again, the high absolute values of the MD strengths are related to the unrealistic high strain rate of the MD tensile tests; thus, the comparison of relative strengths is more useful.

Furthermore, Fig. 4b (the GB MD tensile toughness diagram) offers more critical information about the ductile-to-brittle transition (DBT). The corresponding $\sigma_{\text{UTS}}^{\text{MD}}$ vs. $X/X_{\text{Max}}$ curves at various temperatures are plotted in Fig. 4d. It is shown that the GB can become brittle even with a small amount of Ga addition at low temperatures, but a higher bulk Ga fraction is needed to induce DBT at a higher temperature. When temperature increases to ~0.7$T_m$ or higher, the GB becomes ductile, but the computed $U_T^{\text{MD}}$ is reduced due to the high-temperature softening, which is severe as approaching to the solidus line (Fig. 4b). A DBT line is drawn in Fig. 4b.

It is interesting to further examine the relation between GB structural and mechanical properties. By comparing Fig. 4 with Fig. 3, it is evident that the computed mechanical properties are inversely correlated with GB adsorption. To further investigate this relation, we plot the $\sigma_{\text{UTS}}^{\text{MD}}$ and $U_T^{\text{MD}}$ as functions of $\Gamma_{\text{Ga}}$ at various temperatures. Fig. 4e shows that the computed $\sigma_{\text{UTS}}^{\text{MD}}$ decays with increasing $\Gamma_{\text{Ga}}$ at all temperatures. In addition, the $\sigma_{\text{UTS}}^{\text{MD}}$ vs. $\Gamma_{\text{Ga}}$ curve deceases with increasing temperature uniformly. Fig. 4f shows that the computed $U_T^{\text{MD}}$ always decays with increasing the $\Gamma_{\text{Ga}}$, which is consistent with the well-known Ga segregation in embrittlement. Interestingly, the computed $U_T^{\text{MD}}$ values suddenly drop when $\Gamma_{\text{Ga}}$ reaches a critical value. Notably, this GB DBT occurs at the almost identical value of $\Gamma_{\text{Ga}} \approx 11 \text{ nm}^2$ when temperature is < 700 K (as indicated by the dashed line in Fig. 4e). We denote this critical value of $\Gamma_{\text{Ga}}$ for the DTB as $\Gamma_{\text{Ga}}^{\text{DBT}}$, which will be discussed further in the next section.

To better illustrate the GB segregation-property relation, we replotted computed $\sigma_{\text{UTS}}^{\text{MD}}$ and $U_T^{\text{MD}}$ as functions of GB adsorption $\Gamma_{\text{Ga}}$ (instead of the bulk Ga fraction) and temperature in Fig. 4g and Fig. 4h. Fig. 4g shows that the computed MD strength can be reduced by a combination of increasing Ga segregation and temperature. Notably, the DBT line is almost vertical in Fig. 4h, until significant GB softening takes place at ~0.7$T_m$. The combination of these results shows the DBT is mainly caused and controlled by Ga segregation at low and moderate temperatures.
A Phenomenological Model

Following the Fowler–Guggenheim isotherm for surface adsorption that was adopted by Hondros and Seah for GB segregation, we can express the relation between GB adsorption ($\Gamma_{Ga}$) and bulk Ga fraction ($X$) in an approximation as:

$$\frac{\Gamma_{Ga}}{\Gamma_{Ga}^o - \Gamma_{Ga}} = \frac{X}{1 - X} \exp \left[ -\Delta h_{seg}^{o} + \alpha \left( \frac{\Gamma_{Ga}}{\Gamma_{Ga}^o} \right) \frac{k_B T}{k_B} \right],$$

where $\Gamma_{Ga}^o$ represents the effective total number of the Ga adsorption sites per unit area at the GB, $\Delta h_{seg}^{o}$ is the intrinsic segregation enthalpy (in the dilute limit), $\alpha$ is a parameter to represent interaction between the Ga adsorbates (or Al-Ga pair-interaction), and $k_B$ is the Boltzmann constant. Equation (1) can be reduced to the famous Langmuir-McLean model for $\alpha = 0$. We should note that equation (1) only represents a simplified site-occupying model (as an approximation). Nonetheless, we can fit the hybrid MC/MD simulated GB adsorption $\Gamma_{Ga}$ values (represented in Fig. 3a) with equation (1) and obtain the following parameters:

$$\begin{cases} \Gamma_{Ga}^o = 48.03 \text{ nm}^{-2} \\ \Delta h_{seg}^{o} = -0.113 \text{ eV} \\ \alpha = -0.025 \text{ eV} \end{cases}$$

Here, $\Gamma_{Ga}^o$ represents the “saturation” level of Ga segregation at the GB. The fitted value agrees with the maximal value of ~50 nm$^{-2}$ in the computed GB adsorption diagram (Fig. 3a), but it is substantially above the one monolayer ($\Gamma_{Ga}^M = 8.6$ nm$^{-2}$ for the (110) plane). The negative value of $\Delta h_{seg}^{o}$ indicates that Ga atoms are preferable to segregate at Al GBs. Furthermore, the negative value of $\alpha$ suggests that can lower the segregation enthalpy of Ga with increasing $\Gamma_{Ga}$ to further prompt segregation.

Fig. 5a shows that the parity plot of the $\Gamma_{Ga}$ values predicted by the fitted analytical model vs. MC/MD simulations, which agree well with each other. The calculated root-mean-square error (RMSE) between analytical model prediction and hybrid MC/MD simulations is ~ 3.8 nm$^{-2}$ (~7.6% of $\Gamma_{Ga}^o$). Furthermore, the GB adsorption diagram predicted by the analytical model (Fig. 5b)
shows good similarity to the hybrid MC/MD simulated GB diagram (Fig. 3a) overall, albeit subtle differences in the DBT transition region and near the solidus line.

Based on the analytical model and fitted parameters, we can predict the DBT line. By adopting $\Gamma_{Ga}^{DBT} = 11 \text{ nm}^{-2}$ (the critical value from MD tensile simulations), we calculated the corresponding bulk composition vs. temperature for the DBT line and plotted it as the red dashed line in Fig. 5c, which agree well with hybrid MC/MD simulated DBT line (the purple color in Fig. 5c). Alternatively, we can simply adopt one monolayer adsorption as the DBT threshold: $\Gamma_{Ga}^{DBT} = \Gamma_{Ga}^{ML} \approx 8.6 \text{ nm}^{-2}$ (estimated based on the plane density of the lower-index (110) plane of this $\Sigma 81$ GB). The predicted DBT line (the green dotted line in Fig. 5c) is even closer to the hybrid MC/MD simulated DBT line.

While a simplified analytical model can predict the DBT with reasonable accuracies (Fig. 5), the hybrid MC/MD simulated GB diagrams (Figs. 3 and 4) can still reveal more details for both the structure and composition of the GB complexion and its mechanical properties.

**Discussion**

The computed GB diagram (Fig. 3a) shows Ga excess of Ga can be as high as ~50 nm$^{-2}$, which is about 5.6 Ga monolayers. This suggests the occurrence of Ga multilayer adsorption at the Al general GB. Interestingly, the DBT still occurs at approximately one monolayer level (Fig. 4h). A Fowler-Guggenheim type model with a high saturation level (~5.6 monolayers of pure Ga, which can result in a wider interfacial width with Al-Ga mixing at the GB) and a moderate negative pair-interaction parameter $\alpha$ can fit general trends in the GB adsorption and predict the DBT line reasonably well. The negative fitted $\alpha$ value also suggests the Al-Ga interaction at the GB is preferred over Al-Al and Ga-Ga, which is consistent with the absence of first-order adsorption transition (Fig. 3a) that would occur with a positive $\alpha$.

The general GB adsorption behavior is in contrast to the other classical GBE and LME system, Ni-Bi.$^{13}$ Here, Ga has a large solid solubility in the Al based FCC phase. Thus, the GB segregation can easily go into multilayer region and follow partial order of (i.e., partially occupy the Al sites of) the abutting Al grains, with more disordered segregation at the GB core (Fig. 2). The adsorption transition in the Al-Ga system is continuous with a negative $\alpha$ (i.e., Ga segregation can be more favorable with increasing $\Gamma_{Ga}$). In contrast, Bi has a limited solid solubility in the Ni based FCC
phase. Consequently, the Ni general GBs exhibit Bi bilayer adsorption (i.e., one monolayer on each abutting grain, with little Ni-Bi mixing), which can further undergo reconstruction to form highly-ordered interfacial superstructures.\textsuperscript{28,51} In contrast in Al-Ga ($\alpha < 0$), a first-order adsorption transition occurs in Ni-Bi with a positive pair-interaction parameter (i.e., $\alpha > 0$).\textsuperscript{13}

Notably, this study further constructed GB diagrams of computed mechanical properties, including MD-predicted $U_T^{\text{MD}}$ and $\sigma_{\text{UTS}}^{\text{MD}}$, for the first time to our knowledge. While the specific values predicted from MD tensile tests are expected to differ from experiments due to the high strain rate of the MD tensile simulations, the relative trends, e.g., the DBT and the relatively high-strength region in GB diagrams of computed mechanical properties can offer useful information and prediction. In general, GB diagrams of various other properties can also be constructed via conducting additional simulations on or analyses of the temperature- and composition-dependent the equilibrium GB structures, thereby opening numerous new opportunities.

Conclusions

Using a general GB in a classic GBE/LME system, Ga-doped Al, as our model system, we have extended the computation of GB diagrams from adsorption and interfacial disorder to include GB structural and chemical widths to better represent the structural details of the GB complexion underpinning LME. Most notably, GB diagrams have been further extended to include computed mechanical properties to establish and investigate the unique GB composition-structure-property relationship. Temperature- and composition-dependent GB diagrams can be computed for a spectrum of interfacial thermodynamic, structural, mechanical, and potential other functional properties. This work points to a new direction and paradigm to develop computed GB properties diagrams (beyond the basic thermodynamic characters) that can be generally useful in materials design and materials science, with potentially broad impacts.
METHODS

1. Sample preparation and STEM experiments

We prepared transmission electron micrography (TEM) samples of the Al general GBs with Ga segregation following a well-documented procedure. First, we punched the TEM samples with 3 mm disc from a high-purity (99.99%) Al polycrystalline thin foil (~5 μm in grain size and 100 μm in thickness) by a Gatan disc puncher. The thickness of discs was reduced to ~25 μm by a Gatan disc grinder. The pre-thinned disc was scratched near the center to expose fresh surfaces. Then, we quickly transferred it onto a hot plate at 110 °C and placed a small high-purity (99.999%) Ga particle on the scratched surface to allow the penetration of liquid Ga. The residual oxide particles on the surface were picked by a tweezer to avoid strains in the TEM sample. The sample was sandwiched between two copper rings by glue (G1 glue, Gatan) to prevent hazardous Ga contamination. The reinforced Al disc was thinned by a precision ion polishing system (PIPS; Gatan Model 695) until a hole was drilled by the ion beam. A Thermo Fisher Scientific Talos TEM and a Themis Z aberration-corrected (AC) TEM were used to characterize the atomic-level interfacial structures of randomly selected Al GBs with Ga segregation.

2. Hybrid MC/MD simulation

The GB structures for the simulations were constructed by GBstudio website and Pymatgen code based on coincidence-site lattice (CSL) theory. Two types of GBs, i.e., a symmetric tilt Σ11 (113)/(113) GB and an asymmetric Σ81 (110)/(787) GB of mixed tilt and twist characters (to represent a general GB) were considered in this work. The symmetric Σ11 GB was built based on the STEM image reported in a prior work, which contains 18,480 atoms in the unit cell. The asymmetric Σ81 GB was constructed to mimic an experimentally observed GB randomly selected from a polycrystalline sample in this work. Here, we adopted the low-index (110) surface terminal plane observed in the randomly selected general GB from the experiment. Then, we found a matching high-index plane with a Miller index of (787) to form a CSL with a large Σ value of 81 to satisfy a required periodic boundary condition while better representing a general GB. All subsequent simulations were based on a large unit cell containing 19,440 atoms for the asymmetric Σ81 GB to represent a general GB.

All atomistic simulations were performed using LAMMPS code. An Al-Ga embedded-atom model (EAM) potential originally developed by the Srolovitz group was adopted for all simulations. To test this EAM potential, the Al-Ga bulk phase diagram (Fig. S1 in the Supplementary Information) was simulated, which agreed well with the experimentally measured phase diagram. The simulated Al melting temperature is 925 K (close to the experimental value of 933.5 K with <1% relative error). We note that the calculated maximum solid solubility is slightly higher than experimental value. Such small discrepancies are typical for EAM potentials. We represent our simulation results in the normalized temperature (with respect to the Al melting temperature) and normalized Ga fraction (with respect to the maximum solid solubility). Overall, the agreement suggests the EAM potential is robust and reliable for the Al-Ga system.

The initial GB structure was first relaxed at a high temperature of 700 K for 500 ps with a time step of 0.1 fs by classical MD simulations in constant NPT ensembles. Next, the hybrid Monte Carlo and molecular dynamics (hybrid MC/MD) simulations in isobaric semi-grand canonical (constant N(Δμ)PT) ensembles were carried out to dope Ga atoms into Al GBs at a given temperature and a fixed chemical potential difference Δμ = μ_{Al} − μ_{Ga}, where μ_{Al} and μ_{Ga} is the chemical potential of Al and Ga, respectively. Five MC trial moves were conducted between each MD step with a 0.1 fs MD time step. One million hybrid MC/MD steps were performed for each simulation to achieve convergence.

To construct GB diagrams as a function of temperature (T) and the bulk Ga fraction (X), the hybrid MC/MD simulations were performed from 300 K to 860 K with a temperature step 100 K. At each temperature, a series of MC/MD simulations with increasing Δμ were conducted until the bulk composition of Ga (X_{Ga}) reaches the solid solubility limits. The chemical potential difference Δμ will be converted to bulk Ga fraction based on the hybrid MC/MD simulated equilibrium bulk compositions.
A disorder parameter was calculated for each atom following a procedure proposed by Chua et al. ($\eta_{\text{Dis}} = 0$ for a perfect crystal and $\eta_{\text{Dis}} = 1$ for a perfect liquid). The centrosymmetric parameter (CSP) was calculated by summing the pairs of opposite neighbors of a specific lattice, where the CSP of the ideal crystal CSP is zero due to cancellation of opposite neighbor pairs but crystal defect will have positive CSP values. The atomic structures shown in this work were visualized by the OVITO code.

3. STEM simulation

STEM images were simulated by using the QSTEM program. The hybrid MC/MD simulated Ga-doped Al GB structures was used as the input atomic structures. The thickness of the simulated sample was set to be 3.5 nm (as the thin specimen limit). The scattering semi-angle for HAADF imaging was set to be 70 mrad, the convergence angle was adopted as 15 mrad. The spherical aberration coefficient was set to be 0 μm.

4. MD tensile tests for mechanical properties

Using the hybrid MC/MD simulated equilibrium GB structures, a series of uniaxial tensile tests of GBs were carried out by isothermal-isobaric (constant NPT) MD simulations at desirable temperatures. The strain rate was set to $\sim 5.4 \times 10^9$/s and tensile tests were performed until the final strain reaches ~0.2. See Fig. S2 in the Supplementary Information for representative stress-strain curves at different $\Delta \mu$ values (with different $\Gamma_{\text{Ga}}$) at 300 K. The maximal tensile stress based on the MC/MD simulations was considered as the MD ultimate strength ($\sigma_{\text{UTS}}^{\text{MD}}$). The MD tensile toughness ($U_T^{\text{MD}}$) was calculated by integrating the stress-strain curve (for the strain from 0 to 0.2) based on MD simulations. With an increasing level of Ga doping, the GB first has a ductile behavior, which suddenly becomes brittle when the $\Gamma_{\text{Ga}}$ reaches a critical value.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

CODE AVAILABILITY

The code used to calculate the results of this study are available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

J. L. conceived the idea and supervised the work. C. H. performed the simulations. Y. L. and Z. Y. conducted STEM experiments. C. H. and J. L. wrote the manuscript. All co-authors reviewed and approved the manuscript.

COMPETING INTERESTS

The authors declare no conflict of interests.

ADDITIONAL INFORMATION

Supplementary Information is available for this paper.

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Fig. 1 Validation of the computational approach with ordered segregation at a symmetric tilt GB. a, HAADF STEM of a Ga-doped Al symmetric tilt Σ11 (113)/(113) GB, reprinted from Ref. 33 with permission. b, Simulated STEM images of the same symmetric tilt GB based on the equilibrium atomistic structure obtained from hybrid MC/MD simulations at 300 K and $\Delta \mu = -0.42$ eV. c, The hybrid MC/MD simulated GB structure and the corresponding color maps based on (c) computed disorder parameter ($\eta_{\text{Dis}}$) and (e) centrosymmetric parameter (CSP) on each atom. The 2D averaged (f) Ga atomic fraction ($X_{\text{Ga}}(z); X_{\text{Ga}}(\pm \infty) = X$), (g) disorder $\eta_{\text{Dis}}(z)$, and (h) CSP profiles across the GB as functions of the spatial variable $z$ perpendicular to the GB.
Fig. 2 The structure of general GBs in Al-Ga. a, HAADF STEM of a general GB randomly selected from a Ga-doped Al polycrystalline specimen, where the orientation of the low-index grain surface is (110). b, Simulated STEM images of an asymmetric Σ81 (110)/(787) GB based on the equilibrium atomistic structure obtained from hybrid MC/MD simulations at 300 K and Δμ = −0.4415 eV. c, The hybrid MC/MD simulated GB structure and the corresponding color maps based on the (d) computed disorder parameter (η_{Dis}) and (e) centrosymmetric parameter on each atom. The 2D averaged (f) Ga atomic fraction X_{Ga}(z), (g) disorder η_{Dis}(z), and (h) CSP profiles across the GB as functions of the spatial variable z perpendicular to the GB.
Fig. 3 Computed GB diagrams of thermodynamic and structural characters. The hybrid MC/MD simulated diagrams of (a) adsorption or GB excess of Ga ($\Gamma_{Ga}$) and (b) GB excess of disorder ($\Gamma_{Disorder}$) of the Ga-doped Al asymmetric $\Sigma$81 GB. Computed (d) $\Gamma_{Ga}$ vs. normalized bulk composition ($X/X_{Max}$) and (e) $\Gamma_{Disorder}$ vs. $X/X_{Max}$ curves at various temperatures. The corresponding computed GB diagrams of the (a) effective GB chemical width ($\delta_{GB}^{Chemical}$) and (b) effective GB structural width ($\delta_{GB}^{Structural}$). (c) The GB diagram of the differences between the effective GB structural and chemical widths, where the dashed line denotes $\delta_{GB}^{Structural} = \delta_{GB}^{Chemical}$. 
Fig. 4 Computed GB diagrams of MD simulated mechanical properties. Computed GB diagrams of (a) MD ultimate strength ($\sigma_{UTS}^{MD}$) and (b) MD tensile toughness ($UT^{MD}$) of the Ga-doped Al asymmetric $\Sigma 81$ GB from the MD tensile tests based on the hybrid MC/MD simulated equilibrium GB structures. The computed (c) $\sigma_{UTS}^{MD}$ and (d) $UT^{MD}$ vs. $X/X_{Max}$ curves at various temperatures. The computed (f) $\sigma_{UTS}^{MD}$ and (e) $UT^{MD}$ vs. GB adsorption ($\Gamma_{Ga}$) curves at various temperatures. The corresponding calculated (g) $\sigma_{UTS}^{MD}$ and (h) $UT^{MD}$ diagrams plotted as functions of temperature ($T$) and GB adsorption ($\Gamma_{Ga}$). The lines in Panels (b) and (h) indicate the approximate position of the ductile-to-brittle transition (DBT). The dashed line in Panel (f) indicates the critical threshold of GB adsorption ($\Gamma_{Ga}^{DBT}$) for GB fracture.
Fig. 5 A phenomenological model for fitting GB adsorption and predicting the ductile-to-brittle transition line. 

**a.** Parity plot of model-predicted vs. hybrid MC/MD simulated GB adsorption ($\Gamma_{Ga}$). 

**b.** Model-predicted GB adsorption ($\Gamma_{Ga}$) diagram as a function of $T/T_m$ and $X/X_{Max}$. 

**c.** The ductile-to-brittle transition lines plotted in the $T$-$X_{Ga}$ space from the hybrid MC/MD simulations vs. the model predictions using the critical Ga adsorption values of $\Gamma_{Ga} = \Gamma_{Ga}^{DBT}$ (the critical value from MD tensile tests) and $\Gamma_{Ga} = \Gamma_{Ga}^{ML}$ (monolayer).
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