Monte Carlo simulations of strain-driven elemental depletion or enrichment in Cu$_{95}$Al$_5$ and Cu$_{90}$Al$_{10}$ alloys

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**Abstract**

An interatomic potential for the Cu–Al system based on the modified analytic embedded-atom method was proposed, which provides a reasonable description of the phase stability across the phase diagram. Combining with this potential, Monte Carlo simulations were performed to study strain-induced element segregation and intermixing in bulk and nanostructured Cu$_{95}$Al$_5$ and Cu$_{90}$Al$_{10}$ alloys. Al with a large atomic size is found to segregate to the tensile region while Cu to the compressive region. The elemental depletion or enrichment in dilute or nanostructured alloy is more notable than that in concentrated or bulk one, due to alloy effects or change of local stress. In particular, phase separation in nanostructured alloys leads to a single pure Cu inclusion in the matrix, which will induce strain hardening. The element segregation also affects the chemical ordering that will provide solid-solution strengthening.

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1. Introduction

Elemental segregation and intermixing may alter the structure and local chemical composition of alloys and thus significantly influence their mechanical and chemical properties. It has been demonstrated that the applied compressive, tensile, shear or torsional strain/stress fields can direct the formation of precipitation, ordered compounds, metastable solid solutions, amorphous alloys, patterned nanostructures, and decomposition patterns in the bulk and thin films of binary systems [1–12]. In fact, the kinetics and morphology of segregation or intermixing pattern depend significantly on the heats of mixing, atomic size mismatch, and the nature and magnitude of external mechanical fields [6,8–11]. The complex interplay between the intrinsic thermodynamics (such as heats of mixing and atomic size mismatch) and external mechanical fields is ideally suited for study by simulations, ranging from fully atomistic methods to continuum approaches [1–11].

Cu-based alloys are objects of intensive investigation, due to their excellent plasticity, corrosion resistance, electrical and thermal conductivity. The $\alpha$ phase Cu–Al alloys (with the Al composition less than 19.6 at.%) are the most studied age hardening Cu-based solid solutions. In undeformed state, they exhibit short-range order (SRO) due to the negative heats of mixing, which does not lead to a significant increase in flow stress [13]. In deformed crystals, however, the interactions of segregated solute atoms with lattice defects cause a considerable increase in flow stress. Therefore, $\alpha$ Cu–Al alloys were chosen as model systems since they may exhibit SRO along with solute segregation in deformed state [13], illustrating an example where the nature and magnitude of external strain fields play important roles in tailoring the intrinsic system thermodynamics.

In this work, we first propose an interatomic potential for the Cu–Al system based on the modified analytic embedded-atom method (MAEAM) [14–18]. Then we report its applicability to element segregation in deformed $\alpha$ Cu$_{100-x}$Al$_x$ ($x = 5$ and 10) solid solutions and nanostructured alloys combining with the Monte Carlo (MC) simulations. We also discuss the effect of element segregation on chemical ordering and solute clustering.

2. Theoretical model and simulation details

The system considered here is a Cu crystal with periodic boundary conditions imposed in all three directions, where 5 at.% or 10 at.% Cu atoms are randomly replaced by Al atoms. The simulation cells with strains were shown in Fig. 1. In the bulk alloys, there is a strain region with a width of 5$a_0$ ($a_0$ is the lattice constant of Cu–Al alloy), and two (100) interfaces with fixed uniaxial strains perpendicular to them. For the nanostructured alloys, the compressive strain is radially loaded on the core and the tensile strain is obtained by the free relaxation of atoms in shell region. In order to probe the strain-driven element segregation of $\alpha$ Cu–Al alloys,
we have carried out MC simulations at 300 K and within the NVT ensemble. The advantage of MC method is that the calculation of the equilibrium configurations does not require the details of exact diffusion pathways of atoms in alloys, which may be complex and cooperative in nature. The atomic configurations as shown in Fig. 1 were evolved via (a) atomic positions exchange between two randomly chosen particles with different chemical types and (b) particle displacement in an arbitrary direction for randomly selected single atom. An identity or position switch attempt was accepted or rejected according to the Metropolis criterion [17–19]. In other words, the attempt is accepted when the change in total energy $\Delta E$ is negative; otherwise, it is accepted only if the $\exp(-\Delta E/k_B T)$ is greater than a random number. In this way, the element segregation and atomic relaxation in strained region is possible. On the other hand, the fixed simulation cells, relatively large volume and negligible composition change of bulk region can keep a strain-free bulk, although there is globally atomic exchange and relaxation. The interested physical quantities, such as the distribution of chemical species, are obtained by averaging over 20,000 MC steps within the equilibrated stage (after 10,000 MC steps).

In the present work, the MAEAM potential is used to describe atomic bonding in Cu–Al systems. This potential has already been successfully applied for the study of bulk, surface, and nanoparticles of metals and alloys through incorporating many-body interactions [14–18]. In the framework of MAEAM, the energy of a system can be written as

$$U = \sum_{i=1}^{N} F(\rho_i) + \frac{1}{2} \sum_{j>i} \phi(q_{ij}) + M(P_i)$$

where $F(\rho_i)$ is the embedding energy of atom $i$, a nonlinear function of the electron density $\rho_i$, $\phi(q_{ij})$ is the pairwise potential as a function of the atomic separation $r_{ij}$, $M(P_i)$ is the extra modified term, describing the energy change caused by the nonspherical distribution of atomic electron density. The function forms of $F(\rho_i), \phi(q_{ij})$ and $M(P_i)$ for fcc metals are chosen to be:

$$F(\rho_i) = -F_0 \left[ 1 - n \ln \left( \frac{\rho_i}{\rho_c} \right) \right]$$

$$\phi(q_{ij}) = \sum_{n=1}^{4} k_n \left( \frac{r_{ij}}{r_c} \right)^n$$

$$M(P_i) = -2\pi \rho_i P_i$$

$$\rho_i = \sum_{j=1}^{N} f(r_{ij})$$

$$P_i = \sum_{j=1}^{N} f^2(r_{ij})$$

$$f(r_{ij}) = \frac{f_1}{r_{ij}} \left( \frac{r_{ij}}{r_c} \right)^4 \left( \frac{r_{ij}}{r_e} \right)^2$$

where $\rho_i$ is the sum of electron density $f(r_{ij})$ induced at atom $i$ by all the neighbors within the cutoff distance $r_{ce}$, and $P_i$ is the second order item of electron density $f(r_{ij})$, with their equilibrium values $\rho_c$ and $P_c$, respectively. The cutoff distances of the pair potential function is taken as $r_c = r_s + k_c (r_p - r_s)$, and $r_{ce} = r_p + k_c (r_p - r_s)$ for the electron density function $f(r)$. Here $r_s$ is the nearest neighbor distance, and $k_c$ is an adjustable parameter. Our fitting database includes mainly equilibrium physical properties, such as the lattice parameters, cohesive energy, formation energy of single vacancy, and elastic constants of bulk Al and Cu. The final optimized parameters for Al and Cu are listed in Table 1.

For a binary alloy, we need to determine the cross interaction potential. The heterogenic atomic Cu–Al potential is taken as,

$$\phi_{ab}(r) = \frac{1}{2} \mu \left( \phi_a \left( \frac{r_{fa}}{r_c} \right) + \phi_b \left( \frac{r_{fb}}{r_c} \right) \right)$$

3. Results and discussion

Tables 2 and 3 show the properties of Al and Cu calculated with the fitting parameters, respectively. These properties are compared with available results from density functional theory (DFT)

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Cu</th>
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<td>$k_4$</td>
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Figure 1. (a) Schematic simulation cell for bulk Cu–Al alloy. The box size is $60a_0 \times 12a_0 \times 12a_0$ where $a_0$ is lattice constant. The strain axis is parallel to the $x$-direction. (b) Schematic simulation cell for nanostructured Cu–Al alloy. The box size is $25a_0 \times 25a_0 \times 25a_0$.
The properties of Al calculated with the MAEAM potential in comparison with results from DFT calculations, other simulations, and experiments. Equilibrium lattice parameter $a_0$, cohesive energy $E_c$, formation energy of mono-vacancy $E_{1\text{v}}$, and divacancy $E_{2\text{v}}$, are listed in ev, surface energy $\gamma$ in mJ/m², elastic constants $C$ in GPa.

<table>
<thead>
<tr>
<th>Property</th>
<th>MAEAM</th>
<th>SAEAM [38]</th>
<th>MEAM</th>
<th>TB</th>
<th>DFT</th>
<th>Exp.</th>
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<td>3.543$^{a,b}$</td>
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<tr>
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<td>1.163$^{a,b}$</td>
<td>1.183$^{a,b}$</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>2.016$^{a,b}$</td>
<td>2.15 ± 0.10$^{a,b}$</td>
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<td>$\gamma_{(1\text{1}0)}$</td>
<td>1.407</td>
<td>1.180</td>
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The fits to equilibrium lattice parameter, the cohesive energy, the vacancy formation energy, and elastic constants are quite good for both Al and Cu. It is interesting to note that all EAM-based potentials well reproduce the bulk properties and the anisotropy ratios of surface energy $\gamma_{(1\text{1}0)}/\gamma_{(1\text{1}1)}$ and $\gamma_{(1\text{1}0)}/\gamma_{(1\text{1}1)}$ but usually underestimate the surface energy in comparison with DFT calculations and experimental average values. While TB potential well reproduces the surface energy but not the anisotropy ratios and the bulk properties. That is to say, all these many-body potentials are not satisfactorily transferable from surface to bulk, fitting the parameters to well reproduce the bulk properties often leads to underestimation of the surface energy and vice versa. Herein, we sacrificed some of the accuracy of surface energy to focus on capturing the main features of bulk properties.

For the cross-pair potential function as in Eq. (8), which defines the properties of binary system, the alloying parameters $r_c$ and $\mu$ are taken as 0.260 and 1.000, respectively. The accuracy of the fitting parameters for Cu–Al can be tested by their ability to reproduce and describe the main features of the alloy systems. By using the fitting alloying parameters, some physical properties, such as the heats of formation, the lattice parameters, and dilute heat of solution of binary alloys have been studied. The phase diagram of Cu–Al system is very complex and exhibits many stable or meta-stable intermetallics [38–41]. Fig. 2 shows the heats of formation for disordered solid solution and selected intermetallics in comparison with available experimental, first-principles and semi-empirical potentials data [28,38–41]. The full symbols mean the heats of formation of stable intermetallics while the empty ones stand for metastable phases with the same composition. The phase structures of intermetallics are given in Strukturbericht symbols.

The present MAEAM and the angular-dependent potential (ADP) predict the $\theta$ phase to be more stable than $\delta$ phase at 0 K, consistent with experiments and DFT results. The present MAEAM potential and the EAM potential of Liu et al. [38] predict a better phase stability for Cu-rich compositions than ADP, at the cost of underestimating the energy of the metastable phases. While ADP overestimates the energies of most of the Cu–Al compounds tested [39]. Although none of these potentials exactly reproduces the whole convex hull of the heats of formation provided by DFT calculation, the present potential gives a reasonable description of the global phase stability across the Cu–Al phase diagram. In addition, the fully relaxed dilute heats of solution are −0.815 eV/atom for Al in Cu and −0.105 eV/atom for Cu in Al, consistent with experimental and theoretical data [38,39]. Therefore, present fitting parameters can be used for α Cu–Al alloys with reasonable accuracy.

In order to assess the segregation tendency quantitatively, we first consider the chemical composition in a uniaxial strain region within bulk. Fig. 3 shows the concentration depth profiles of Cu$_9$Al$_{10}$ within a series of uniaxial tensile or compressive strains. It is clear that Al atoms segregate to the tensile slab region and Cu atoms enrich (Al deplete) obviously in the compressive region. The results also suggest that the elemental segregation in

![Table 2](image)

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![Fig. 2](image)

The heats of formation for disordered solid solution and selected intermetallics in comparison with available experimental, first-principles and semi-empirical potentials data [28,38–41]. The full symbols mean the heats of formation of stable intermetallics while the empty ones stand for metastable phases with the same composition. The phase structures of intermetallics are given in Strukturbericht symbols.

![Fig. 3](image)

The concentration depth profiles of the Cu$_9$Al$_{10}$ bulk alloy under a series of compressive or tensile strains. The dash-dotted line stands for the perfect bulk composition. The insert figures show the typical configurations of deformed bulk alloys.
thermodynamic equilibrium state is sensitive to the nature and magnitude of external strains, indicating a higher strain provides greater driving force for elemental segregation. Although the diameter of an Al atom (0.286 nm) is about 12% larger than that of a Cu atom (0.255 nm), the heat of mixing is −0.055 eV/atom for undeformed Cu_{90}Al_{10} alloy. Thus, the chemical energy gained by forming SRO in alloys overcomes any elastic energy changes obtained by elemental segregation. For a deformed bulk, as the extrinsic strains increase, the imposed strain is reduced in segregated state where atoms can partially reduce elastic mismatch strains more effectively and thus satisfy their bonding preference. When Al atoms move to the strain region, they prefer the tensile sites, leading to the enrichment of large atoms (Al) and the release of strain energy. Similarly, the strain energy due to misfit is much relieved by small atoms (Cu) segregating to compressive sites. A similar segregation of large (small) atoms to the local tensile (compressive) strains field was also observed in alloy systems with negative heats of mixing [42–46]. Smaller Cu atoms in Al–Cu alloys were observed to segregate to the compressive regions of the extended dislocation dipole [42]. In Al–Mg alloys, larger Mg atoms segregation to the tensile strain field of a split edge dislocation was observed, where the area below the stacking fault is under tension [43–45]. It also demonstrates that the precise composition and size control of nanostructures can be achieved by careful design of applied strain fields. For example, the coexistence of tensile and compressive strains by applying periodic indenters on the top and bottom surfaces of binary thin films can lead to highly ordered nanostructures such as nanocomposites [7–11].

In the ultrafine-grained or nanocrystalline materials fabricated by severe plastic deformation [47–49], tensile and compressive strains may coexist locally near grain boundaries (GBs) as well as triple junctions and interact with each other in a complicated way. Herein a simplified model is applied to make a further understanding of compositional rearrangements in nanostructured alloys. In Fig. 4 the resulting atomic configurations and radial composition profiles are plotted as a function of shells positions for nanostructured Cu_{90}Al_{10} alloys with a series of radial compressive strains. There is a clear indication that the Cu segregation level depends upon the three-dimensional hydrostatical compressive strains. The tendency of Cu or Al enrichment is very similar to but more pronounced than that under uniaxial strains. It demonstrates that elemental segregation level depends in nature upon the change of local volume that is closely related to the change of local pressure. For example, a uniaxial compressive strain of −2% results in −2% change in volume, while a −2% hydrostastical compressive strain results in about −6% change in volume. Thus, it is easy to understand that the strain energy is more relieved by smaller atoms (Cu) moving to the compressive core region of the nanostructured alloys than to the corresponding slab ones. Similar enrichment and phase segregation in bulk Al_{90}Mg_{10} with hydrostastical compression were predicted by MC simulation and the extended Langmuir–McLean equation [43]. It was found that shear strains (up to 5%) had no effect on the solute concentration when the Al_{90}Mg_{10} bulk was subjected to simple shear (zero volume change), confirming the above deduction of volume change dependence of the elemental segregation level. Enrichment of larger atoms Mg at high-angle GBs as well as triple junctions and depletion of Mg in internal regions near GBs were experimentally observed and further theoretically explained in ultrafine-grained Al–Mg alloys [49,50]. Mg segregation locates in the tensile regions of GBs created by full extrinsic dislocations, which can pin dislocation segments and thereby hinder dislocation emission and increase the yield strength of the alloys. Furthermore, an interesting phenomenon has been found that Cu–Al elemental segregation under certain compressive strain will lead to phase separation. As shown in Fig. 3, the phase separation results in a single Cu nanometer-sized inclusion in the compressive core of the matrix, which needs to be further verified with experiment. The inclusion-matrix system, where a relatively hard inclusion (Cu-like) embedded in a relatively soft matrix (solid solution-like), is expected to hinder the motion of dislocations nucleated under compression and thus induce strain hardening [5].

The segregation behaviors for all simulated systems are summarized in Fig. 5, where the normalized segregation compositions are plotted as a function of the applied strains. The segregation of Cu_{90}Al_{10} is also presented to gain some insight into the effect of global alloy composition. The normalized composition, a, is given as $a = (c_{i} – c_{i}^{c})/c$, where $c_{i}$ is the local average Al concentration in the strain region and $c$ is the global average Al concentration. A positive value of $a$ denotes Al segregation, while a negative value indicates Cu segregation. The dashed line in this figure at $a = 0$ indicates no segregation, while $a = -1$ is for phase separation. Both in bulk and nanostructured materials, the segregation tendency of Cu_{90}Al_{10} is similar to that of Cu_{90}Al_{10}, but there are more pronounced Cu or Al segregation under the same magnitude of strains, which comes from the alloying effect. The calculated heat of mixing is −0.030 eV/atom for Cu_{90}Al_{10} alloy and −0.055 eV/atom for Cu_{90}Al_{10} by using present potentials. Therefore, the elemental

![Fig. 4](image-url) The radial distribution of the Al concentration of the Cu_{90}Al_{10} nanostructured alloy under a series of compressive strains. The dash-dotted line stands for the perfect bulk composition. The insert figure shows the typical configuration of deformed nanostructured alloys.

![Fig. 5](image-url) The dependence of the average normalized composition on the strain for both bulk and nanostructured Cu_{90}Al_{10} and Cu_{90}Al_{10} alloys. The dash-dotted lines stand for the perfect mixing and phase separation.
segregation of Cu$_{50}$Al$_{50}$ solid solutions is more pronounced than that of Cu$_{85}$Al$_{15}$ ones with the weaker Cu–Al bonding. Aside from elemental segregation, SRO or solute clustering is an additional configuration change. In the present work we characterize SRO using the Warren–Cowley (WC) order parameter [51]. The WC order parameters in strained region are plotted as a function of neighbor shell number in Fig. 6. It suggests that some degree of SRO exists in all the simulated alloys, where the first nearest-neighbor shells preferentially contain heterogeneous atomic pairs and the second nearest-neighbor ones preferentially contain homogeneous ones. Beyond the first and second shells, these correlations decrease and the alloys exhibit a more random distribution of pair types. It is also apparent that the degree of ordering generally increases with increasing Al composition. These are in good agreement with three-dimensional X-ray diffuse scattering investigations and MC simulations, where small ordered domains were detected and this effect increases markedly with increasing Al content in undeformed alloys [52,53]. Similar evidence of SRO and even ordered phase below an edge dislocation were also found in Al–Mg solid solution [43,45].

Combining the information of SRO and atomic distribution, we found that most of the solute in the alloy is involved in atomic clustering. We propose that the SRO or clustering solute will provide significant solid-solution strengthening. Firstly, the solute clusters can contribute to significant strengthening, thereby providing effective resistance to slip dislocations, as well as to strain hardening and ductility, by increasing the dislocation storage capability [12,42–45,46]. In fact, solute clustering has long been reported in conventional α Cu–Al alloys as well as nanostructured Al alloys engineered by severe plastic deformation and linked to strengthening [12,13,47]. Furthermore, the dislocations may be stabilized by forming Cottrell atmosphere-like solute clustering at the dislocation cores. The interactions of dislocations with solute atoms may cause a considerable increase in flow stress of deformed alloys [13,42–45].

It should be pointed out that the present model of strain test is somewhat simplistic to capture the details of element segregation and chemical ordering in nanostructured alloy. For example, it does not include the effects of shear strain, grain size and orientation accompanying in real conditions. In a system with negative heats of mixing, simple (zero volume change) shear strain (up to 5%) has no effect on the solute concentration [43], but severe shear deformation can produce clear chemical ordering in both the crystalline and amorphous phases [6]. It was also verified that in the system under plastic deformation, the size and orientation of grains could affect the mixing process and the degree of mixing [3,5]. Furthermore, no kinetics of segregation or ordering can be obtained from present model as the system evolves without taking into account actual diffusion of atoms or vacancies. However, conventional atomic-scale simulations are always hindered by the heavy computational cost or the complex diffusion barriers which are sensitive to local chemical environment and strain field [54]. While more realistic simulations are needed for the full evaluation of the strain effects and kinetic effects, it is predicted that there will be atomic segregation in bulk and nanostructured alloy under aforementioned local strains.

4. Conclusions

The cross-interaction function of Cu–Al alloys based on MAEAM potential was fitted, which gives reasonable trends of phase stability across the Cu–Al phase diagram. Strains-induced atomic segregation and chemical ordering in α Cu–Al alloys were investigated using this potential combined with Metropolis MC method. Our calculations show that the compressive region tends to be enriched with small atoms like Cu and contrarily the tensile one tends to be enriched with large atoms like Al. These are generally in agreement with the experimental and other theoretical results. We found that the same trends hold in dilute and nanostructured alloys, but solute depletion or enrichment is more notable than in concentrated or bulk ones due to alloy effects or change of local pressure, respectively. In particular, phase separation in nanostructured alloys leads to a single pure Cu inclusion in the matrix, which will induce strain hardening. The strain-induced elemental segregation also affects chemical ordering in α Cu–Al alloy, which will provide significant solid-solution strengthening. All the evidence collected in the present work points out an intimate coupling between atomic sizes, chemical composition and external strains on element segregation and chemical ordering. The simulation results suggest that applying strains allows for the control of composition, structure and properties of a number of alloy systems with various intrinsic thermodynamics.

Acknowledgments

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References


