Identifying interatomic potentials for the accurate modeling of interfacial segregation and structural transitions

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ABSTRACT

Chemical segregation and structural transitions at interfaces are important nanoscale phenomena, making them natural targets for atomistic modeling, yet interatomic potentials must be fit to secondary physical properties. To isolate the important factors that interatomic potentials must capture in order to accurately model such behavior, the performance of four interatomic potentials was evaluated for the Cu-Zr system, with experimental observations used to provide validation. While experimental results show strong Zr segregation to grain boundary regions and the formation of nanoscale amorphous complexions at high temperatures and/or dopant compositions, a variety of disparate behaviors can be observed in hybrid Monte Carlo/molecular dynamics simulations of doping, depending on the chosen potential. The potentials that are able to recreate the correct behavior accurately reproduce the enthalpy of mixing as well as the bond energies, providing a roadmap for the exploration of interfacial phenomena with atomistic modeling. Finally, we use our observations to find a reliable potential for the Ni-Zr system and show that this alloy should also be able to sustain amorphous complexions.

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1. Introduction

Grain boundaries are important planar defects that influence a variety of material behaviors such as creep resistance, densification during sintering, fracture, fatigue, and thermal stability [1–6]. The structure and chemistry of grain boundaries can be altered by solute segregation, allowing material properties to be tuned and optimized by a method sometimes called "grain boundary segregation engineering" [7,8]. Such a framework can be used to enhance the creep resistance of nanostructured alloys, as shown by Darling et al. [9] for nanostructured Cu-10 at.% Ta. These alloys contained Ta nanoclusters at the grain boundaries between Cu crystals and exhibited creep rates which were 6–8 orders of magnitude lower than most of reported data for other nanocrystalline metals. The concept of segregation engineering has also been applied to accelerating sintering by Park and Schuh [10], who observed the formation of Cr-rich phases between W-rich particles during the sintering of W-15 at.% Cr compacts. These Cr-rich regions acted as rapid transport pathways for W diffusion and thus reduced the sintering temperature and time needed for consolidation to full density. Raabe and coworkers [7,11,12] reported a nanoscale phase

transformation from martensite to austenite due to Mn segregation in an Fe-9 at.% Mn maraging steel, showing that this interfacial phase transformation led to an increase of impact toughness. In addition to the examples of phase separation shown above, segregating dopants can also facilitate the formation of "complexions," or interfacial states whose existence depends on the adjacent crystals [13–15]. Dillon et al. [14] reported six types of discrete complexions, categorized by complexion thickness, in doped and undoped alumina. Khalajhedayati and coworkers [16,17] applied this concept to nanostructured metals, where nanoscale amorphous complexions were observed in Cu-Zr alloys, and these amorphous intergranular films dramatically improved the ductility of the material without sacrificing strength.

Most of the research studies mentioned above were in some way combined with atomistic modeling to explore the physical mechanisms responsible for the behavior observed in experiments. For instance, Darling and coworkers [9,18] found that the bowing of grain boundaries at Ta clusters observed in experiments could be confirmed by molecular dynamics simulation and was consistent with a Zener pinning model. In addition, experiments can have limitations on what can be measured or contain a convolution of many factors that are difficult to separate. For example, Khalajhedayati et al. [16] showed that amorphous complexions were formed in nanocrystalline Cu-Zr but also found that complexion thickness varied significantly at different boundaries.

Unfortunately, high resolution electron microscopy is limited to interfaces that can be viewed edge on, meaning a complete categorization of boundary structures in the material is extremely difficult, if not impossible, experimentally. However, Pan and Rupert [19] were able to provide a fundamental understanding of boundary-to-boundary variations in complexion thickness by building bicrystalline models for hybrid Monte Carlo/molecular dynamics simulations. These authors showed that different grain boundaries vary in their ability to collect Zr dopants and transition to an amorphous complexion at different global Zr compositions. These variations can explain the variety of boundary thicknesses seen in an experiment for a single global Zr composition. As another illustrative example, Frolov et al. [20] reported on interesting filled-kite and split-kite structures at $\Sigma 5$ (3 1 0) and $\Sigma 5$ (2 1 0) grain boundaries in pure Cu, predicting a transition between them under certain conditions which would be difficult to isolate experimentally.

While these examples demonstrate the value of atomistic modeling, these simulations are only as reliable as the potentials used to represent atomic interactions. Typically, the choice of interatomic potential is guided by experimental data and/or first-principles calculations. In some cases, the relevant material properties or defect energies of interest are obvious. For example, a direct fit to anisotropic elastic moduli can be used if elasticity is of interest [21], while fitting to the experimental phase diagram will allow precipitation and phase separation to be modeled [22]. In other cases, it is more difficult to isolate the essential properties to be fit for accurate simulation, particularly when a given phenomenon is not directly related to an equilibrium thermodynamic parameter in the bulk. For instance, Dziedzic et al. [23] focused on the structure and mass transport properties of liquid Al-Cu alloys and compared three distinct potentials by their ability of reproducing total and partial pair correlation functions, densities, angular distribution functions, coordination numbers, and self-diffusion coefficients. These authors found that two of the potentials failed to produce reasonable melting temperatures or densities of the targeted alloys, as well as missing the mark on other important properties, and thus were not appropriate for their study. However, even the potential which reproduced these properties still had difficulty reproducing local chemical ordering in an accurate manner. Similarly, Malerba et al. [24] tested the efficacy of four potentials for modeling radiation damage in Fe. These authors found that interatomic potentials fitted to first-principles forces (i.e., the slopes of potential-energy surfaces) or liquid structure factors (i.e., pair correlation functions) were able to more closely match available first-principles data for point defect formation and migration, key behaviors of interest when simulating radiation damage. However, for interfacial segregation and structural transitions, no guidelines currently exist for the selection of a suitable potential. The majority of the interesting mechanisms are occurring at the grain boundary region, yet most potentials are created using the equilibrium properties of bulk phases.

In this paper, we test different interatomic potentials for the Cu-Zr system with the goal of creating guidelines for potential selection to enable the accurate simulation of interfacial phenomena and structural transitions. Four interatomic potentials are chosen for this task, covering a range of functional forms and physical properties used for fitting. A set of new experimental observations on sputtered Cu-Zr thin films that are shown here, as well as past literature reports [16,17], demonstrate that (1) Zr should exhibit a strong tendency to segregate to the grain boundaries and (2) amorphous intergranular films with stable nanoscale thicknesses should be created at high temperatures and high Zr concentrations. These experimental reports provide a baseline for comparison of the different potentials that are studied. We find that the functional form of the interatomic potential is less critical than the choice of

properties chosen for fitting. Specifically, the enthalpy of mixing and the bond energies must be faithfully represented to predict the chemical segregation and transition to an amorphous intergranular film. This can be done multiple ways, as one of the reliable potentials was created by fitting the ab initio atomic forces from a variety of atomic configurations while the other was created by calibrating to the liquid enthalpy of mixing and diffraction data from amorphous alloys. Armed with these guidelines, we extend our work to another promising system, Ni-Zr alloys, finding that amorphous films can be formed but that Zr only weakly segregates to the interfaces.

2. Methods

2.1. Experimental materials processing and characterization

Cu-Zr alloy films (composition of Cu-4.3 at.% Zr) were deposited onto Cu substrates with magnetron co-sputtering at a temperature of 400 °C and an Ar pressure of 1.5 mTorr in an Ulvac JSP 8000 metal deposition sputter tool. All samples were sealed under vacuum in high purity quartz tubes and annealed under vacuum at 500 °C for 24 h to promote grain growth and the segregation of dopants to the grain boundary, followed by a one-minute annealing treatment at 900 °C (0.92 $T_{solidus}$) to encourage grain boundary premelting. The samples were then rapidly quenched by being dropped into water to preserve any phases or grain boundary complexions occurring at high temperature. Transmission electron microscopy (TEM) samples were made from the films using the focused ion beam (FIB) lift-out technique [25] on an FEI dual beam Quanta 3D microscope using Ga+ ions. High resolution TEM (HRTEM) and energy-dispersive X-ray spectroscopy (EDS) were performed on an FEI Titan at 300 kV. Fresnel fringe imaging (FFI) was used to identify grain boundary films and to ensure edge-on orientation with respect to the grain boundary. A more detailed experimental study of complexion formation in a variety of Cu-rich films can be found in Ref. [26].

2.2. Computational methodology

Bicrystal models containing two $\Sigma 5$ (3 1 0) grain boundaries were used as starting configurations. A $\Sigma 5$ (3 1 0) grain boundary has a small, repeating kite-shaped structure (shown in Fig. 1) that allows for a reasonable simulation cell size, yet can act as a representative high-angle and high-energy grain boundary. Periodic boundary conditions were applied in all directions during the simulations. The simulation box has a length of approximately 23 nm (X direction), height of 11 nm (Y direction), and thickness of 4 nm (Z direction) containing 95,520 atoms. A hybrid Monte Carlo/molecular dynamics simulation method was used to simulate grain boundary segregation and any subsequent structural transitions [27]. This technique has been successfully used to model phase transformation and grain boundary segregation in earlier work. For example, Koju et al. [18] used Monte Carlo/molecular dynamics methods to study the Cu-Ta system and observed the formation of Ta-rich clusters at the grain boundary, a finding which was consistent with experimental observations in Cu-Ta [9]. Classical molecular dynamics simulations controlled the structural relaxation and were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package with an integration time step of 1 fs [28]. An isothermal-isobaric (NPT) ensemble with the Nose-Hoover thermostat/barostat was applied to relax samples at two temperatures (600 K and 1000 K) under zero pressure. To find chemical equilibrium, Monte Carlo simulations in a variance-constrained semi-grand canonical ensemble were performed after every 100 molecular dynamics steps.