Regular article

Formation of ordered and disordered interfacial films in immiscible metal alloys

Zhiliang Pan [a], Timothy J. Rupert [a,b,*]

[a] Department of Mechanical and Aerospace Engineering, University of California, Irvine, CA 92697, USA
[b] Department of Chemical Engineering and Materials Science, University of California, Irvine, CA 92697, USA

A B S T R A C T

Atomistic simulations are used to study segregation-induced intergranular film formation in Cu—Zr and Cu—Nb alloys. While Cu—Zr forms structurally disordered or amorphous films, ordered films comprised of a second phase usually precipitate in Cu—Nb, with a critical nucleation size of ~1 nm below which the ordered phase cannot form. While the ordered film is retained at high temperature for a low energy Σ11 (113) boundary, a disordering transition is observed for a high energy Σ5 (310) boundary at low dopant concentrations. Finally, the effect of free surfaces on dopant segregation and intergranular film formation is investigated for both alloys.

© 2016 Published by Elsevier Ltd on behalf of Acta Materialia Inc.

Many important material properties such as fracture and corrosion are dominated by interfacial phenomena [1], meaning that control of interface structure would be extremely advantageous for better materials design. Complexions are interfacial features that are in thermodynamic equilibrium with their abutting phases and which have a stable, finite thickness [2]. Complexions and transitions between different complexion types have been shown to be responsible for such diverse behavior as abnormal grain growth [3], solid-state activated sintering [4], liquid-metal embrittlement in Ni—Bi [5], and a dramatic increase in the ductility of nanocrystalline Cu—Zr [6]. Complexions can be classified in many ways, but a popular formulation is the Dillon-Harmer complexion type [3] where higher numbers are assigned to thicker complexions which generally have increased levels of adsorbate. Dopants in monolayer, bilayer, or trilayer complexions form specific segregation patterns at the grain boundary (GB), while nanoscale intergranular films and wetting phases can be either structurally and chemically ordered or disordered [2]. GB pre-melting [7,8] and amorphous intergranular films (AIFs) [3,9] are examples of higher level complexions which exhibit both chemical and structural disorder.

Since dopant segregation and GB transitions are nanoscale phenomena, atomistic simulations are ideal tools for studying complexion formation. For example, molecular dynamics (MD) have been used to study the structure of calcium silicate intergranular films in silicon

nitride crystals [10]. Atomistic Monte Carlo (MC) methods have also been used to study the pre-melting behavior of GBs in Cu—Ag alloys [11]. Frolov et al. used a hybrid MC/MD method to discover two different ordered complexions that can exist at a Σ5 (210) symmetric tilt GB in Cu—Ag [12]. The transition between these two complexion types occurred when the dopant concentration was increased for a fixed temperature. Frolov et al. also showed that variation of the number of atoms in the grain boundary plane, provided by the addition of a free surface in an MD simulation, could drive a structural transition even in GBs of pure Cu [13]. Recently, Pan and Rupert used atomistic simulations to study disordering transitions in Cu—Zr [9], finding that different ordered complexions first form, with the Dillon-Harmer type depending on the boundary's starting structure, and then a transition to a structurally disordered state occurs at high interfacial concentrations of Zr. Purely thermodynamic models for complexion formation have also been developed. For example, Luo and Shi performed a study on disordering in binary alloys, showing that equilibrium complexion diagrams can be created to see the effects of temperature and global dopant concentration on complexion formation [14]. Frolov and Mishin also developed a generalized thermodynamic theory which showed that up to four interface phases can be supported in a binary single-phase system [15]. However, the range of structural and chemical order that can be accessed in intergranular films is not well understood. All of the examples listed above which treated intergranular films describe disordered or amorphous complexions. It is not clear if that is a foregone conclusion, with the abutting crystal frustrating crystallization of the intergranular film for nanoscale thicknesses, or if this observation is merely a function of the alloys that have been studied to date. There is

* Corresponding author at: Department of Mechanical and Aerospace Engineering, University of California, Irvine, CA 92697, USA.
E-mail address: trupert@uci.edu (T.J. Rupert).

also no clear understanding of the competition between dopant segregation and complexion formation on GBs and surfaces.

In this paper, hybrid atomistic MC/MD simulations were used to study GB doping and complexion transitions in Cu—Zr and Cu—Nb alloys, in order to develop a better understanding of nanoscale intergranular film formation. These binary systems are both immiscible combinations, where the dopant wants to segregate to interfacial regions, but they differ in other thermodynamic features, such as heat of mixing and the existence of stable intermetallic phases. Specifically, Cu—Nb has a positive enthalpy of mixing [16] and is a poor glass former, so it should be difficult for disordered complexions to form in this system. We find that the Cu—Zr system only forms amorphous films whereas the Cu—Nb system usually forms ordered intergranular films through heterogeneous nucleation. However, at higher temperatures, a disordering transition is observed for Cu—Nb under certain conditions. The competing effect of free surfaces is also studied, showing that surface segregation and structural transition also occurs for Cu—Zr.

Hybrid MC/MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code [17], with all MD simulations using a 1 fs integration time step. The interatomic potential for Cu—Zr system was developed by Mendelev et al. [18], with Cu—Cu and Zr—Zr interactions described using embedded-atom method (EAM) potentials and Cu—Zr interactions with a Finnis-Sinclair formulation. The Cu—Nb interactions were described using an EAM potential that is able to rebuild the main features of the experimental phase diagram in both solid and liquid states [16]. Bicrystals with two different tilt GBs were used as starting configurations so that the effect of GB character can be studied. One sample contains two Σ11 (113) GBs, with GB energy of 0.022 eV/Å². The other sample contains two Σ5 (310) GBs, with GB energy of 0.062 eV/Å². Each simulation cell is about 20 nm long, 20 nm tall, and 4–5 nm thick, with each containing ~200,000 atoms. Periodic boundary conditions were applied in all three directions for the majority of simulations, but only in the length and thickness direction when studying the effect of free surfaces.

The samples were first equilibrated with a conjugate gradient minimization technique to the minimum potential energy state and then further relaxed with a Nose-Hoover thermos/barostat for 20 ps under zero pressure at 600 K and 1200 K. The doping with Zr or Nb solutes was then simulated using the MC method in a variance-constrained semigrand canonical ensemble [19] after every 100 MD steps, with the global composition of dopants fixed to different values. In this MC scheme, the chemical potential difference was given an initial guess

and then adjusted during the simulation to achieve the required composition. However, the final composition can slightly deviate from the target value, with the deviation depending on how much the initial guessed chemical potential difference deviates from the authentic one for the simulated system. The acceptance probability and thus the speed of MC simulation also decreases due to this mismatch [19]. To solve this problem, the initial chemical potential difference was also adjusted every 10 MC steps based on the difference between the achieved and target global compositions. The initial chemical potential difference is increased if the achieved composition is lower than the target value and decreased otherwise. With this modified MC scheme, the authentic chemical potential difference can also be achieved, which is, in fact, the guessed value at the converged MC step. Here the MC/MD simulation is considered to be converged if the fitted slope of the system potential energy over the last 4000 MC steps is less than 0.001 eV/step. After equilibrium, another conjugate-gradient minimization technique was used to remove thermal noise in the grain interior and at the same time preserve the interfacial structure obtained during the doping process. Atomic configurations are visualized using an open-source visualization tool OVITO [20], with the local structure identified using adaptive common neighbor analysis (CNA) [21,22]. Face centered-cubic (FCC) atoms are colored green, hexagonal close packed atoms red, body-centered cubic (BCC) atoms blue, icosahedral atoms yellow, and other atoms white. The volume of each atom is also calculated using Voronoi tessellation method to measure the average GB thickness.

Fig. 1 shows doping of the Cu—Zr and Cu—Nb alloys for the Σ11 boundary at 600 K, which is only ~48% and ~44%, respectively, of the solidus temperature for binary alloys in each system [23,24]. The frame on the left of each figure part shows the local structure of each atom, while the frames on the right in each part show the chemical distribution. GB segregation of the dopant species occurs in both systems, as shown in Fig. 1(a) and (d), yet there is a clear difference between the Nb and Zr induced structural transitions at the GB. The Cu—Zr alloy forms AIFs, as shown by the prevalence of atoms which could not be assigned a common crystal structure in Fig. 1(b) and (c). This is a typical segregation-induced GB premelting or transition from an ordered complexion to a disordered one, as extensively discussed in the literature [2,25–27]. Increased dopant concentration leads to a thickening of this disordered region, consistent with prior reports of both Cu—Zr [9] and Cu—Ag [11] alloys. Cu—Nb, on the other hand, forms an ordered, crystalline phase at the GB through heterogeneous nucleation. It is essential to note that this phase is not a complexion, but
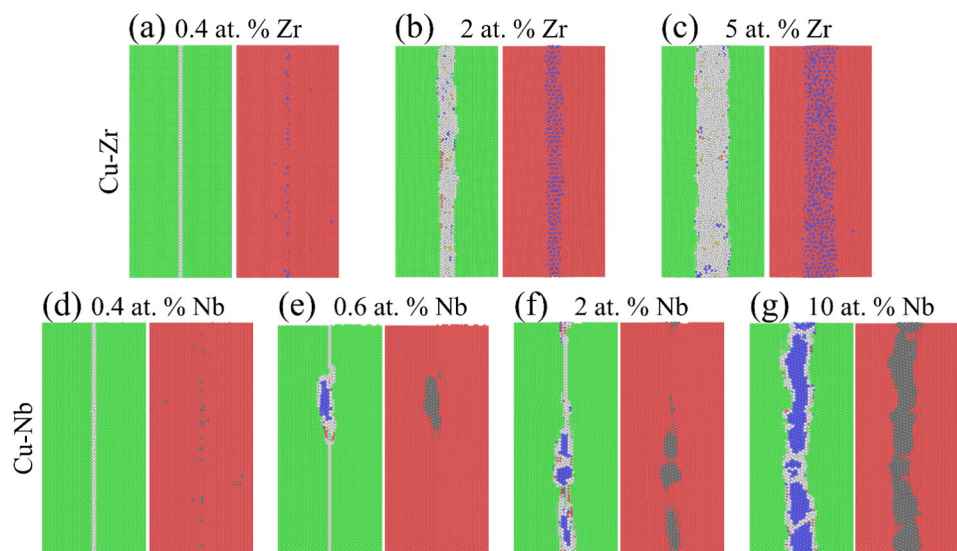

Fig. 1. Atomic snapshots of one of the two Σ11 (113) GBs in the sample, doped at 600 K in (a)–(c) the Cu—Zr and (d)–(g) Cu—Nb systems with periodic boundary conditions. The left frame in each pair shows the local structure of the atoms colored according to CNA. The right frame shows the chemistry of the boundary where peach atoms are Cu, blue atoms are Zr, and gray atoms are Nb. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)