Acta Materialia 117 (2016) 91–99

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Computational study of metallic dopant segregation and embrittlement at molybdenum grain boundaries

Richard Tran, Zihan Xu, Naixie Zhou, Balachandran Radhakrishnan, Jian Luo, Shyue Ping Ong*

Department of NanoEngineering, University of California San Diego, La Jolla, CA 92093, USA

ARTICLE INFO

Article history:
Received 4 March 2016
Received in revised form
14 June 2016
Accepted 3 July 2016

Keywords:
DFT
Embrittlement
Strengthening
Grain boundary segregation
Molybdenum

ABSTRACT

Mo and its alloys have been widely used as refractory materials owing to their excellent high temperature properties, but a critical limitation is their low ductility. Doping the grain boundaries (GBs) of Mo with metals such as Zr or Al have previously been demonstrated as a promising approach to address this shortcoming, whereas other alloy elements are known to embrittle the GBs. In this work, we investigated the segregation and strengthening/embrittling effects of 29 metallic dopants at the Σ5(310) tilt and Σ5(100) twist Mo GBs using density functional theory (DFT) calculations and empirical continuum models. In agreement with previous works for other metals, we find that the strain, as measured by the relative metallic radius versus Mo, is a good predictor of the segregation tendency, while the difference in cohesive energies between the dopant and Mo is a good predictor of the strengthening/embrittling effect. However, we find that dopant chemistry also plays a significant role in affecting segregation behavior at GBs, particularly in driving the formation of intermetallic precipitates or 2-D interfacial phases (complexions). We also show that the site preference of a dopant in the GB can lead to strengthening effects that deviate from those predicted using simple bond-breaking arguments. Assuming a fast cleavage model of fracture, Ta, Re, Os and W are predicted to have a weak strengthening effect on Mo for the Σ5(310) tilt GB, and Mn, Fe, Co and Nb are predicted to have reasonable strengthening effects for the Σ5(100) twist GB.

1. Introduction

Mo [1] and its alloys [2] have been widely used in high temperature applications [3] owing to their excellent stability, strength, high thermal and electrical conductivity [4], and a low coefficient of thermal expansion [5]. In addition, its high creep, corrosion, and sputtering resistance opens up applications in medical devices [6] and coatings for aerospace and defense components [7]. However, Mo still suffers from low ductility at near room temperatures [8,9].

It is well known that segregation of alloying elements or impurities at grain boundaries (GBs) leads to embrittling effects in Mo as well as many other alloys [10–14]. Nonetheless, doping with certain other elements can also be a promising approach to mitigate the low ductility of Mo, as demonstrated by Miller et al. [15] for Zr, Al, C and B dopants in 2002 Charai et al. [16]. also investigated liquid metal wetting embrittlement (LME) of Pb, Sn and Ni on Mo GBs and showed that the wettability by Pb and Ni is dependent on crystallography or GB types. More recently Liu et al. [8], reported a nanostructuring technique that involves a molecular-level liquid-liquid mixing/doping to achieve yield strengths over 800 MPa and tensile elongation as large as 40% at room temperature in Mo alloys. On the computational front, first principles investigations of dopant segregation and diffusion in Mo GBs have been carried out with light elemental dopants such as B, C, N, O and H [17,18]. In particular Janisch and Elsässer [17], used local-density functional theory (LDFT) to confirm one of the predictions made by the empirical Cotrell model [19] by showing that the bonding strength between Mo GBs and its interstitial dopants depends on the strength of hybridization due to the relative position of electronic bands and thus on the valence configuration of the elements.

GBs in metals critically affect their mechanical properties by acting as centers of dopant segregation [20,21] and system stabilization [22]. Although GB segregation in other metals, such as Fe [23], W [24], and Ni [25,26], have been extensively studied, a

* Corresponding author.
E-mail address: ongsp@ucsd.edu (S.P. Ong).

http://dx.doi.org/10.1016/j.actamat.2016.07.005
1359-6454/

systematic first principles investigation of metallic dopant segregation in Mo GBs is yet to be carried out.

In this work, we performed density functional theory (DFT) calculations to investigate segregation and strengthening phenomena in the Σ5(310) symmetric tilt and Σ5(100) twist GBs of Mo for 29 metallic dopants. We compared the results of our investigation with those computed from the empirical Miedema [27] and McLean [28] models. We will discuss whether segregation and strengthening/embrittling effects can be explained using simple models based on strain and cohesive energy, and the reasons for observed deviations from these models.

2. Methods

For brevity, the terms "twist GB" and "tilt GB" will henceforth be used to refer to the Σ5(100) twist and Σ5(310) tilt GBs investigated in this work. All GB model construction, input file generation and analyses were performed using the Python Materials Genomics (pymatgen) library [29]. The following subsections outline the various structural models and calculation parameters used. Comprehensive convergence tests were carried out (see Fig. S1 in Supplementary Information) to ensure that the relevant properties of interest (*e.g.*, segregation energy) were converged to within 0.02 eV using these models and parameters.

2.1. GB structural models

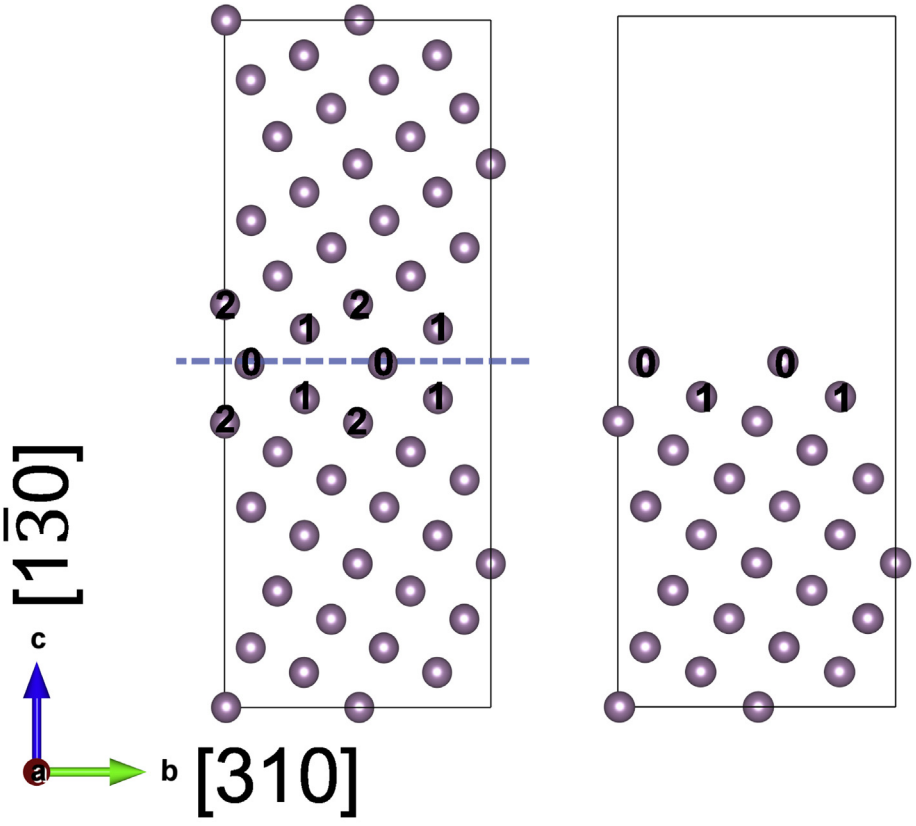
GB structures were generated from the fully relaxed body-centered cubic (bcc) Mo unit cell with cubic lattice parameter $a = 3.167$Å. The tilt GB model (Fig. 1(a)) had dimensions 9.443 Å × 9.956 Å × 24.760 Å with 144 atoms, and the twist GB model (Fig. 2) had dimensions 7.083 Å × 7.083 Å × 25.343 Å with 80 atoms. The twist GB model was generated in accordance to coincidental site lattice (CSL) theory [30]. Free surface calculations were performed using cells of the same cell sizes as the GB models, but with approximately half the numbers of atoms.

2.2. DFT calculations

All DFT calculations [31,32] were performed using the Vienna Ab initio Simulation Package (VASP) [33] within the projector augmented wave (PAW) [34] approach. The exchange-correlation effects were modeled using the Perdew-Berke-Ernzerhof (PBE) generalized gradient approximation (GGA) [35] functional, and all calculations were spin-polarized. A plane wave cutoff energy of 400 eV and a Gamma-centered *k*-point mesh were used for all calculations. The energies and atomic forces of all calculations were converged to within 5×10^{-4} eV and 0.02 eV Å^{-1} respectively. The Methfessel-Paxton method [36] was chosen as the smearing algorithm, the blocked Davidson iteration scheme [37] was chosen as the electron minimization algorithm, and ions were updated with the conjugated gradient algorithm. Γ-centered *k*-point meshes of $6 \times 6 \times 1$ and $7 \times 7 \times 1$ were chosen for the tilt and twist boundary structures, respectively.

2.3. Key parameters for segregation studies

From DFT calculations, the grain boundary (GB) and free surface



(a) View along *a* axis. (b) (310) surface slab.

Fig. 1. Structure model for (a) the Mo Σ5(310) tilt GB and (b) the Mo (310) surface slab. Symmetrically distinct sites in the tilt GB are numbered with increasing integers representing increasing distance from the mirror plane.