First-principles study of energy and atomic solubility of twinning-associated boundaries in hexagonal metals

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Abstract—Twinning-associated boundaries (TB), $\{10\bar{1}n\}$ coherent twin boundaries (CTB) and the coherent basal–prismatic (CBP) boundary in six hexagonal metals (Cd, Zn, Mg, Zr, Ti and Be) are studied using first-principles density function theory, with the focus on the structural character of TB and the solute's solubility at TB. Regarding the structure and energy of TB, the formation of TB is associated with the creation of an excess volume. All six metals show positive excess volume associated with $(10\bar{1}1)$ and $(10\bar{1}3)$ CTB, but the excess volume associated with $(10\bar{1}2)$ CTB and CBP can be positive or negative, depending on the metal. The $(10\bar{1}2)$ CTB has higher excess energy than $(10\bar{1}1)$ and $(10\bar{1}3)$ CTB for metals with $c/a < \sqrt{8/3}$, but lower for metals with $c/a > \sqrt{8/3}$. More interestingly, CBP has lower excess energy than $(10\bar{1}2)$ CTB for all metals. This is consistent with the recent finding concerning the pure-shuffle nucleation mechanism of $(10\bar{1}2)$ twins. To understand solubility at TB, the solubility of solute atoms in Mg, Ti and Zr is calculated for solute positions in bulk, $(10\bar{1}2)$ CTB and CBP boundaries. In general, solute atoms have better solubility at CTB and CBP than in bulk. Interestingly, the solubility of solute atoms changes linearly with normal strain at CBP, increasing with normal strain for solute atoms with a greater metallic radius than the matrix, and decreasing with normal strain for solute atoms with a smaller metallic radius than the matrix. This suggests that the distribution of solute atoms in bulk, CTB and CPB boundaries varies with stress state and, in turn, affects the mobility of TB.
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1. Introduction

Hexagonal materials with hexagonal close-packed (hcp) crystal structure, such as Cd, Zn, Mg, Zr, Ti and Be, are widely used as structural materials in many industries, ranging from transport and energy to biomedical applications, owing to their low density, high specific strength and stiffness, good machinability and superior damping capacity [1–3]. Magnesium and its alloys, the lightest structural materials, have attracted the attention of the automotive industry for reducing the vehicle's weight to increase its efficiency and reduce the emission of greenhouse gas [4]. Titanium (Ti) can be alloyed to produce strong lightweight alloys for aerospace, military and other applications [5]. Zirconium (Zr) has excellent resistance to corrosion and is often used in aggressive environments [6]. However, hexagonal materials lack the ductility and formability of cubic materials, owing to a scarcity of easy slip systems and the localized shear characteristic of twinning. Taking Mg as an example, basal $\langle a \rangle$ slip ($\{0001\}\langle 11\bar{2}0 \rangle$) is the major dislocation-based plastic deformation mechanism at room temperature [7]. The non-basal slip deformation

mechanisms, such as prismatic $\langle a \rangle$ slip ($\{10\bar{1}0\}\langle 11\bar{2}0 \rangle$) and pyramidal $\langle c+a \rangle$ slip ($\{11\bar{2}2\}\langle \bar{1}\bar{1}23 \rangle$), are relatively difficult to activate, because of the high resistance at low temperatures [8,9]. To accommodate arbitrary deformation under mechanical loading, $\{10\bar{1}2\}\langle 10\bar{1}1 \rangle$ twins are commonly activated at room temperature [7–12]. However, the localized shear associated with twinning is partly behind the low ductility and the poor deformability of Mg alloys [13–17]. In addition, the presence of twin boundaries (TB) causes a crystallographic discontinuity of slip systems across TB. Consequently, a high resolved shear stress is required to transmit a dislocation across TB, thereby strengthening the material [18–21]. Atomistic simulations have provided insight into the interactions of TB with lattice glide dislocations in connection with both the kinetics and the energetics of slip transmission across TB [22–26].

The current emphasis for advancing the application of hexagonal materials is to improve their deformability while preserving high flow strength. The techniques to improve their formability are mainly through tuning the relative activity of basal slip, non-basal slip and twinning [27]. It has been thoroughly documented that the strength and ductility of alloys are influenced by solute content on solid-solution hardening [28,29]. Improving the mechanical properties of hexagonal metal alloys necessitates a fundamental understanding of the microstructure–property relations at

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different length scales, from atomic [30–32] to continuum level modeling [33,34]. There have been many studies on the interaction between solute atoms and the motion of dislocations at the atomic level [30–32]. At moderate or elevated temperatures, where solute diffusion is significant, the elastic interactions between solutes and dislocations lead to solute segregation and depletion around dislocations and the formation of a so-called Cottrell atmosphere [35]. Such a solute atmosphere produces a drag force on moving dislocations, which can pin the dislocation motion [35,36].

Besides solute pinning on dislocations, the pinning effect of solute atoms on TB has attracted attention recently [37,38]. The coherent twin boundary (CTB) associated with a twin plane is a highly symmetric interface between two crystals, often with one crystal the mirror image of the other. The two crystals share atoms in CTB at regular intervals. This is a much lower-energy and thermally stable interface than grain boundaries that form when crystals of arbitrary orientation bond together. Nie et al. [37] recently reported that segregation of solute atoms at CTB reduces the local strain at CTB and helps pin the twin motion. For the twinning mode $\{10\bar{1}2\}\langle10\bar{1}1\rangle$, two different TB have recently been recognized, $(10\bar{1}2)$ CTB and the basal-prismatic (BP) [39–41] boundary (or the prismatic-basal (PB) boundary). Twinning processes (nucleation, propagation and growth), experimental observations and atomistic simulations suggest that CTB are responsible for twin propagation and growth associated with the glide of twinning dislocation [36,42,43], while the BP/PB boundary is involved in twin nucleation via a pure-shuffle nucleation mechanism [39] and in twin growth via migration of the BP/PB boundary [39–41,44]. These TB have distinctive structures that may lead to different solubility of solute atoms. In addition, owing to their crystallography, the BP/BP boundary experiences a normal stress (compression or tension) when a CTB is subject to a shear stress associated with twinning [41]. This difference in stress state may further change the solubility of solute atoms among TB and, in turn, change the distribution of solute atoms at TB. Thus, a precise knowledge of the chemistry, structure and properties of TB and solute solubility at TB is crucial to understand and control the twinning activity for improving the mechanical properties of hexagonal metals.

This paper studies the structure and energy of four $\{10\bar{1}n\}$ CTB and BP/PB boundaries in six hexagonal metals (Cd, Zn, Mg, Zr, Ti, Be) and the solubility of solute atoms at $(10\bar{1}2)$ CTB and BP boundaries in Mg, Ti and Zr using density functional theory (DFT). First, the essential details of the DFT calculations are described. Section 3 focuses on the structure and energy of twinning-associated boundaries in six hexagonal metals. It was found that the formation of a twin boundary is associated with the creation of an excess volume. Section 4 studies the solubility of solute atoms in Mg, Ti and Zr with respect to the solute position in bulk, CTB and PB/BP boundaries. The results provide an insight into the selection of solute atoms for tailoring the twin response in different hcp metals. Finally, the conclusions regarding TBs' structure and the solubility of solute atoms in Mg, Ti and Zr are presented.

2. Method

Atomic-scale simulations, including molecular statics/molecular dynamics (MS/MD) and ab initio DFT, have proved to be a valuable tool in recent decades for studying the character and stability of structural defects, and the energetic and kinetics aspects of defect nucleation, reactions and interactions [45–50]. MS/MD simulations use an empirical potential to model the interatomic forces, and have the capability of handling the motion of millions to billions of atoms on nanosecond timescales [51,52]. However, accurate empirical potentials are not available for most hexagonal metals or for binary systems. Ab initio electronic structure calculations that can predict interatomic forces, energies and structural stability with very precise accuracy were used in the present study.

Six hexagonal metals were studied, Cd, Zn, Mg, Zr, Ti and Be, using the VASP code [53,54]. Generalized gradient approximation was used for the exchange correlation functional with the Perdew–Becke–Erzenhof [55] parameterization, and projector augmented wave pseudopotentials for the interaction between valence electrons and ionic cores [56,57]. The number of valence electrons in pseudopotentials is 2 ($2s^2$) for Be, 2 ($3s^2$) for Mg, 4 ($4s^2$, $3d^2$) for Ti, 4 ($5s^2$, $4d^2$) for Zr, 12 ($4s^2$, $3d^1$) for Zn and 12 ($5s^2$, $5d^{10}$) for Cd. The plane wave cutoff was chosen to be 500 eV. An optimized structure was obtained when the force on each atom was <0.0001 eV nm^{-1}. By means of a $19 \times 19 \times 11$ Γ-centered Monkhorst–Pack [58,59] k-point mesh to sample the Brillouin zone of the primitive unit cell of hcp crystal structure, lattice constants of six hexagonal metals were obtained that are in very good agreement with the experimental values (Table 1). With these lattice constants, the structure and energy of twinning-associated boundaries in a fully periodic bi-crystal model, and solubility of solute atoms in Mg, Ti and Zr with respect to solute position in bulk, CTB and PB/BP boundaries were studied further. The computational details are described in the corresponding sections.

3. Excess volume and energy of twinning-associated boundaries

3.1. Coherent TB

To characterize the structural character and excess energy of CTB, a fully periodic bi-crystal model was constructed, containing two identical coherent TB for DFT calculations as follows. For example, in the case of $(10\bar{1}2)$ CTB, a single crystal containing 11 atomic planes of $(10\bar{1}2)$ as the matrix was first created (Fig. 1a). The x axis of the matrix is along the zonal direction $[1\bar{2}10]$, the y axis is along the $[\bar{1}011]$ direction, and the z axis is along the $[10\bar{1}2]$ direction. Then, the twinned crystal was created, using the mirror image of the matrix about the lower mirror plane of $(10\bar{1}2)$ (referred to as the mirror plane M_1). Note that a $(10\bar{1}2)$ plane contains atoms from A and B sites (which are located at the y–z plane with the interplanar spacing of $a/2$ along the x direction and shown by circles and triangles, respectively), and thus is not atomic flat with a height difference of D between A and B sites in the z direction. The mirror x–y planes (M_1 and M_2) are in the middle of the A and B sites along the z direction. Fig. 1b shows the detail of the atomic arrangement near the mirror plane M_1. The mirror image of the matrix is shown by solid symbols for clarity. Fig. 1c shows the atomic configuration of a bi-crystal that contains two identical CTB after mirroring the matrix and bonding them together. Since the two