First-principles Study of Energy and Atomic Solubility of Twinning-associated Boundaries in Hexagonal Metals

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Abstract

Using first-principles density function theory, we studied twinning-associated boundaries (TBs), $\{10\bar{1}n\}$ coherent twin boundaries (CTBs) and the coherent basal-prismatic boundary (CBP) in six hexagonal metals (Cd, Zn, Mg, Zr, Ti and Be), with the focus on structural character of TBs and solute's solubility at TBs. Regarding structure and energy of TBs, the formation of TBs is associated with creation of an excess volume. All the six metals show positive excess volume associated with $(10\bar{1}1)$ and $(10\bar{1}3)$ CTBs, but the excess volume associated with $(10\bar{1}2)$ CTBs and CBP can be positive or negative depending on metal. $(10\bar{1}2)$ CTB has higher excess energy than $(10\bar{1}1)$ and $(10\bar{1}3)$ CTBs 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 TBs, we calculated solubility of solute atoms in Mg, Ti, and Zr 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, solubility of solute atoms linearly changes with normal strain at CBP, increasing with the normal strain for solute atom with a greater metallic radius than the matrix, and decreasing with the normal strain for solute atom with a smaller metallic radius than the matrix. This suggests that the distribution of solute atoms in bulk, CTB, and CBP varies with stress state, and in turn affects mobility of TBs.

Keywords: first principles, twin boundary, solubility, hexagonal metals

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1. Introduction

Hexagonal materials with hexagonal close packed crystal structure, such as Cd, Zn, Mg, Zr, Ti, Be, are widely used as structural materials in many industries ranging from transport and energy to biomedical applications due 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 under aggressive environment [6]. However, hexagonal materials lack the ductility and formability of cubic materials due to 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 ($\{11\bar{2}\bar{2}\}\langle \bar{1}\bar{1}23 \rangle$), are relatively difficult to be activated because of the high resistance at low temperature [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 causes a crystallographic discontinuity of slip systems across twin boundaries (TBs). Consequently, a high resolved shear stress is required to transmit a dislocation across TBs, thereby strengthening the material [18-21]. Atomistic simulations have provided insight into the interactions of TBs with lattice glide dislocations in connection with both the kinetics and the energetics of slip transmission across TBs [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 different length scales, from the atomic [30-32] to the continuum level modeling [33-34]. There has been a lot of study to understand the interaction between solute atoms and 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 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 twin boundaries 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 CTBs reduces the local strain at CTB and helps pin the twin motion. For the twinning mode $\{10\bar{1}2\}\langle 10\bar{1}1\rangle$ two different twin boundaries have been recently recognized, $(10\bar{1}2)$ CTBs and the Basal-Prismatic [39-41] (BP) boundary (or the Prismatic-Basal boundary PB). Twinning processes (nucleation, propagation and growth), experimental observations, and atomistic simulations suggest that CTB is 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 TBs have distinctive structures that may lead to different solubility of solute atoms. In addition, due to their crystallography, the BP/BP boundary experiences a normal stress (compression or tension) when CTB is subject to a shear stress associated with twinning [41]. This difference in stress state may further change solubility of solute atoms among TBs and, in turn, change the distribution of solute atoms at TBs. Thus, a precise knowledge of the chemistry, structure, and properties of TBs and solute's solubility at TBs is crucial to understand and control the

twinning activity for improving the mechanical properties of hexagonal metals.

In this paper, we study structure and energy of four $\{10\bar{1}n\}$ CTBs and BP/PB boundaries, in six hexagonal metals (Cd, Zn, Mg, Zr, Ti, Be) and solubility of solute atoms at $(10\bar{1}2)$ CTB and BP boundaries in Mg, Ti and Zr using Density Functional Theory (DFT). We first describe the essential details of our Density Functional Theory calculations. In section 3, we focus on structure and energy of twinning-associated boundaries in six hexagonal metals. We found that the formation of twin boundary is associated with creation of an excess volume. In section 4, we study solubility of solute atoms in Mg, Ti, and Zr with respect to solute position in bulk, CTBs, and PB/BP boundaries. The results provide insight into selection of solute atoms for tailoring the twin response in different HCP metals. Finally, we present our conclusion regarding TBs' structure and solubility of solute atoms in Mg, Ti, and Zr.

2. Method

Atomic-scale simulations, including molecular statics/molecular dynamics (MS/MD), and *ab-initio* density functional theory, have proven over the past decades a valuable tool for studying 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 capability of handling the motion of millions to billions of atoms on nanosecond time scales [51-52]. However, accurate empirical potentials are not available for most hexagonal metals or for binary systems. In our study, we used *ab-initio* electronic structure calculations that can predict interatomic forces, energies, and structural stability with very precise accuracy.

We studied six hexagonal metals, Cd, Zn, Mg, Zr, Ti, Be, using the VASP code [53-54]. We used generalized gradient approximation (GGA) for the exchange correlation functional with the Perdew-Becke-Erzenhof (PBE) [55] parameterization, and PAW pseudopotentials for the interaction between valence electrons and ionic cores [56-57]. The number of valence electrons in pseudopotentials are 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 is chosen to be 500 eV. An optimized structure was obtained when the force on each atom is smaller than 0.0001 eV/nm. Using 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 hexagonal close packed crystal structure, we obtained lattice constants of six hexagonal metals that are in very good agreement with the experimental values (Table I). With these lattice constants, we further studied 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, CTBs, and PB/BP boundaries. The computational details will be described in the corresponding sections.

3. Excess volume and energy of twinning-associated boundaries

3.1 Coherent Twin Boundaries

To characterize structural character and excess energy of CTBs, we construct a fully periodic bi-crystal model containing two identical coherent twin boundaries for DFT calculations as follows. For example, in the case of $(10\bar{1}2)$ CTB, we first create a single crystal containing 11 atomic planes of $(10\bar{1}2)$ as the matrix (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 we create the twinned crystal using the mirror image of the matrix about the lower mirror plane of $(10\bar{1}2)$ (referred as the mirror plane M_1). Note that a $(10\bar{1}2)$ plane contains atoms from A and B sites (that 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 Δ 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 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 CTBs after mirroring the matrix and bonding them together. Since the two crystals share atoms in the CTB, the last step is to determine the positions of atoms at the CTB (shown in black in Fig. 1d) by averaging the coordinates of atoms belonging to the two crystals. Finally, the dimensions of the unit simulation cell are equal to a along the x-

axis and $\sqrt{3a^2 + c^2}$ along the y-axis. The dimension for both the twinned and matrix crystals along the z-axis vary with the material. We tested the dependence of interface excess energy on the size along the z-axis by varying the dimension from 20 to 40 twin planes and found that the difference in the interface excess energy is less than 5 mJ/m² (the error bar is less than 4%). To save computation cost, the simulation cell contains 9 twin planes for both the matrix and the twinned crystals and two identical CTBs. Using the same procedure, we constructed (10 $\bar{1}$ 1) and (10 $\bar{1}$ 3) CTBs.

To obtain a minimum energy twinned structure one can directly relax the bi-crystal under zero internal stresses constraint, but the accuracy is numerically limited by the stresses accuracy. Here, we adopted a straining method to directly compare the system energy with respect to structure change. By varying the interplanar spacing ($d_l = d_0 \pm \delta$) between the first atomic planes of the two crystals, as shown in Fig. 2a, we increase or decrease the dimension of the bi-crystal model along the z-axis, 2δ , associated with the change in the first interplanar spacing. When δ is equal to zero, the bi-crystal model has the same volume as a perfect single crystal. A bi-crystal model with a non-zero δ is equivalently strained with respect to the zero-spacing model. The strained bi-crystal is fully relaxed under fixed boundary dimensions till the force on each atom is smaller than 0.0001 eV/nm. The minimum energy structure among structures with different δ corresponds to the equilibrium, relaxed twin structure. DFT calculations were performed for six hexagonal metals with a $19 \times 11 \times 3$ Γ -centered Monkhorst Pack k-point mesh. Fig. 2b shows the change in excess energy as a function of δ for (10 $\bar{1}$ 2) CTBs. Interestingly, we found that the energy minimum does not correspond to $\delta = 0$ for either of the metals studied. This suggests the creation of an excess volume associated with the formation of CTB. For example, the minimum energy for Zr and Ti is at negative values of δ , whereas for Cd, Zn and Be minimum energy is at positive values of δ . This could be due to broken symmetry at CTB that results in change in local bonding associated with the redistribution of electron density different from the bulk. For the structure corresponding to the minimum energy, we further characterized the influence region from the CTB based on the change in the interplanar spacing. We found that the excess volume is delocalized within 4-5 atomic planes from the CTB (Fig. 2c and 2d).

For example, the interplanar spacing in the first atomic layer is greater than that in the bulk for Mg, but smaller for Zr. These results are consistent with earlier calculations done by Serra and Bacon [60] using empirical potentials for hcp metals, where they also found excess volume in the vicinity of twin planes.

The other two coherent twin boundaries $(10\bar{1}1)$ and $(10\bar{1}3)$ are studied using the same method. DFT calculations were performed for six hexagonal metals with a $19 \times 7 \times 5$ Γ -centered Monkhorst Pack k-point mesh. Fig. 3a and 3b show the change in interface excess energy as a function of δ for $(10\bar{1}1)$ and $(10\bar{1}3)$ CTBs. The minimum in these curves indicates that the formation of $(10\bar{1}1)$ and $(10\bar{1}3)$ CTBs is always associated with creation of a positive excess volume, which is delocalized within a few atomic planes from the CTB.

The formation energy of a coherent twin boundary is calculated with $\gamma_{CTB} = (E_{CTB} - E_{bulk})/2A$ at the minimum energy state. E_{CTB} is the total potential energy of the twinned bi-crystal model, E_{bulk} is the potential energy of a bulk single crystal containing the same number of atoms, A is the area of the twin boundary and the factor 2 accounts for the two identical boundaries in the simulation model. The results are summarized in Table II and show good agreement with previous calculations [37, 49-50].

3.2 Coherent BP/PB Boundary

The study of coherent BP/PB boundary (CBP/CPB) is complicated due to the lattice mismatch between the basal and the prismatic planes. According to the orientation relation, the interface bonds a basal plane of one crystal (referred to as basal-crystal) and a prismatic plane of the other crystal (referred to as prismatic-crystal). The basal-crystal adopts a coordinate system, x-axis along $[1\bar{2}10]$, y-axis along $[\bar{1}010]$ and z-axis along $[0001]$. For the prismatic-crystal, x-axis along $[1\bar{2}10]$, y-axis along $[0001]$ and z-axis along $[\bar{1}010]$ as shown in Fig. 4a. The periodicity along x-axis is equal for both crystals and can form a coherent structure. However, the periodicity along y-axis for the two crystals is different, $\sqrt{3}a$ for the basal-crystal and c for the prismatic-crystal. To make a coherent BP interface, we applied strain ε_{yy} in the y-direction to both crystals. The final

periodicity along y-axis is equal to $(\sqrt{3}a + c)/2$, resulting in the applied strain $\varepsilon_{yy}^{basal} = \frac{2(\sqrt{3}a - c)}{\sqrt{3}a + c}$ for the basal-crystal and $\varepsilon_{yy}^{prism} = \frac{2(c - \sqrt{3}a)}{\sqrt{3}a + c}$ for the prismatic-crystal (Fig. 4b). We determined the periodicity L_z^{basal} and L_z^{prism} along z-axis for the two crystals by relaxing the basal-crystal and prismatic-crystal under zero normal stress σ_{zz} with fixed periodicities along the x and y axes. The interplanar spacing of the z-plane is equal to $d_{basal} = L_z^{basal}/2$ in the basal-crystal and $d_{prism} = L_z^{prism}/2$ in the prismatic-crystal. The interplanar spacing d_0^{BP} between the basal plane and the prismatic plan is chosen as $(d_{basal} + d_{prism})/2$, which corresponds to zero excess volume in the BP bi-crystal. The BP bi-crystal model is composed of a basal-crystal (10 basal planes) and a prismatic-crystal (10 prismatic plane) that forms two identical BP interfaces (Fig. 4b). By varying the interplanar spacing $d^{BP} = d_0^{BP} \pm \delta$ at the two BP interfaces, we created a series of strained BP bi-crystals and relaxed them using a $19 \times 11 \times 3$ Γ -centered Monkhorst Pack k-point mesh until the force on each atom is smaller than 0.0001 eV/nm. Fig. 4c shows the change in interface excess energy as a function of δ , indicating a positive excess volume for Be and negative excess volume for Zn, Cd, and Zr.

The formation energy of a coherent BP/PB boundary is calculated as $\gamma_{CBP} = (E_{CBP} - E_{bulk} - E_{elas}^{basal} - E_{elas}^{prism})/2A$, where E_{CBP} is the total potential energy of the bi-crystal containing two coherent BP boundaries, E_{bulk} the bulk energy, E_{elas}^{basal} is the elastic energy stored in the basal-crystal, E_{elas}^{prism} is the elastic energy stored in the prismatic-crystal and A is the area of the BP boundary.

3.3 Remarks about CTBs and CBP

Table II summarizes interface excess energies of the three CTBs and CBP for the six metals. $(10\bar{1}2)$ CTB has higher formation energy than $(10\bar{1}1)$ and $(10\bar{1}3)$ CTBs for Mg, Zr, Ti and Be ($c/a < \sqrt{8/3}$), but lower for Cd and Zn ($c/a > \sqrt{8/3}$). For the twinning mode $\{10\bar{1}2\} \langle 10\bar{1}1 \rangle$ observed in most hexagonal metals, the high interface energy implies that such twins must be activated because the smaller shear displacement makes them kinetically preferred over other twin modes. More interestingly, $(10\bar{1}2)$ CTB has higher formation energy than CBP/CPB for all metals. This is consistent with the

recent finding associated with pure-shuffle nucleation mechanism of $(10\bar{1}2)$ twin [39] where a twin nucleus is primarily outlined by CBP/CPB instead of $(10\bar{1}2)$ CTB.

4. Solubility of solute atoms in Hexagonal Metals

We calculated and compared solubility of solute atoms (with metallic radius greater or smaller than the hexagonal metal) in Mg, Ti, and Zr with respect to solute position in bulk, $(10\bar{1}2)$ CTB and CBP/CPB boundaries, respectively. We also studied the influence of the stress state, characteristic of CTB and CBP/CPB boundaries, on solubility of solute atoms at TBs.

In what follows, we describe the details for solubility in Mg, briefly summarize the major results for Ti and Zr, and finally make remarks of solubility at TBs according to the results in Mg, Ti, and Zr.

4.1 Solute solubility in Mg

(a) Solubility in bulk. We used a periodic $3 \times 2 \times 3$ super-cell consisting of 72 atoms with the x direction along $[1\bar{2}10]$, the y direction along $[10\bar{1}0]$ and the z direction along $[0001]$. One solute atom was introduced in the single crystal by substitution of one Mg atom (corresponding to solute concentration of 1.41%). DFT calculation was performed with a $9 \times 7 \times 5$ G-centered K-point mesh. The solubility of solute atoms in the bulk Mg is calculated as

$$\Delta E_{sol}^{bulk} = \frac{E^{sol}(Mg_{(N-m)}, X_m) - E^{bulk}(Mg_{(N-m)}) - E^{bulk}(X_m)}{m} \quad (1)$$

Where $E^{sol}(Mg_{(N-m)}, X_m)$ is the total energy of a system consisting of $(N-m)$ Mg atoms and m solute (X) atoms, $E^{bulk}(Mg_{(N-m)})$ is the bulk energy of $(N-m)$ Mg atoms and $E^{bulk}(X_m)$ is the bulk energy of m solute atoms. The solubility for 20 solute atoms with different metallic radius arranged in ascending order is plotted in Fig. 6a and summarized in Table III. Cd shows the highest solubility in bulk and K the lowest.

(b) Solubility at coherent twin boundary. The solubility of solute atoms at $(10\bar{1}2)$ CTB

was computed in a bi-crystal model that consists of 84 atoms (Fig. 5a). The dimensions of the model have two periodicities along the x direction, one periodicity along the y direction and 21 (10 $\bar{1}2$) planes along the z direction. The top and bottom two atomic planes in the upper and lower crystals are fixed. At a (10 $\bar{1}2$) CTB, there are two atomic sites, A and B along the x-axis. By substituting one atom in A or B site, we calculated the solubility of solute atom with the planar concentration of 25%. The planar concentration is based on the ratio of solute atom to the total atoms in the twin plane. DFT calculations were performed using a 11 $\times$ 11 $\times$ 3 G -centered k-point mesh. The solubility of solute atoms at CTB is calculated as:

$$\Delta E_{sol}^{CTB} = \frac{E^{twin}(Mg_{(N-m)}, X_m) - E^{twin}(Mg_{(N-m)}) - E^{bulk}(X_m)}{m} \quad (2)$$

where $E^{twin}(Mg_{(N-m)}, X_m)$ is the total energy of the twinned bi-crystal containing $(N-m)$ Mg atoms and m solute (X) atoms, and $E^{twin}(Mg_{(N-m)})$ is the total energy of the twinned bi-crystal containing $(N-m)$ Mg atoms. The results are plotted in Fig. 6a and summarized in table III. Solutes with smaller radius than Mg favor A-sites at CTB and solutes with larger radius than Mg favor B-sites at CTB.

(c) **Solubility at coherent BP/PB boundary.** The solubility of solute atoms at CBP was computed in a bi-crystal model that consists of 80 atoms (Fig. 5d). The dimensions of the model have two periodicities along the x direction, one periodicity along the y direction and 20 atomic planes (10 basal planes and 10 prismatic planes) along the z direction. The top and bottom two atomic planes in the upper and lower crystals are fixed. At a CBP boundary, solute atom can either occupy an atomic site in the prismatic plane or in the basal plane. DFT calculations were performed using a 9 $\times$ 11 $\times$ 3 G -centered k-point mesh. The solubility of solute atoms at CPB is calculated as:

$$\Delta E_{sol}^{CBP} = \frac{E^{CBP}(Mg_{(N-m)}, X_m) - E^{CBP}(Mg_{(N-m)}) - E^{bulk}(X_m)}{m} \quad (3)$$

where $E^{CBP}(Mg_{(N-m)}, X_m)$ is the total energy of the PB/BP bi-crystal containing $(N-m)$ Mg atoms and m solute (X) atoms, and $E^{CBP}(Mg_{(N-m)})$ is the total energy of the bi-crystal containing $(N-m)$ Mg atoms. The results are plotted in Fig. 6b and summarized in

table III. Solutes with smaller radius than Mg favor prismatic layer at BP boundary, and solutes with larger radius than Mg favor basal layer at BP boundary.

(d) ***Variation of solubility with the normal strain at the BP boundary:*** Using high-resolution transmission electron microscopy (HRTEM) and atomistic simulations, structures of $(10\bar{1}2)$ deformation twin boundaries have been characterized to consist of $(10\bar{1}2)$ CTBs and BPs/PBs. According to this structural feature, the propagation of $(10\bar{1}2)$ twins is accomplished through either the glide-shuffle mechanism of twinning dislocations or the climb-shuffle mechanism of BP/PB boundary [40-41]. Under a shear stress along the twinning direction on the twin plane, the BP/PB boundary is subject to normal stress, compression or tension depending on the type of BP, as shown in Fig. 7a. In addition, the excess volume associated with TBs will result in a local strain on the boundary. Therefore, it is to be expected that the solubility of solute atoms at these boundaries will be affected by local and normal strains.

We studied variation of solubility with normal strain at CBP boundary for four solute atoms, Ge, Zn, Ce, and La that have a good solubility at CTB and BP/PB boundaries in Mg. We applied a uniaxial strain along the normal of the BP boundary in a range from -1% to 1%. Fig 7b shows change in segregation energy, defined as the difference between solubility at the boundary and in the bulk, as function of normal strain at the BP boundary. We found that solubility of atoms with a bigger metallic radius than Mg (Ce, La) decreases as the normal strain goes from compression to tension, but solubility of atoms with a smaller metallic radius than Mg (Ge, Zn) is larger for tensile normal strain. Thus, under the same shear stress on CTB, solutes have different solubility in BP and PB boundaries, indicating that BP and PB boundaries will be doped at different extent and may have different mobility. More interestingly, the normal strain can switch the order of solubility at CTB and BP/PB boundaries. For example, solubility of Ge and Zn is better at CTB than BP/PB boundaries at zero strain but under compressive strain of ~1 and 2% respectively their solubility at BP/PB becomes better than at CTB.

4.2 Solute solubility in Ti and Zr

Using the same procedure as discussed above for Mg, we calculated solubility of

solute atoms in Ti and Zr with respect to solute position in bulk, CTB and BP/PB boundaries.

The solubility of 14 solute atoms in Ti is plotted in Fig. 8a and summarized in table IV. For clarity, we only show the minimum solubility of solute atoms at CTB and BP boundaries. We found that atoms with smaller metallic radius than Ti are soluble in bulk as well as at TB and BP boundaries. However, with the exception of Indium, all solutes that have metallic radius larger than Ti are neither soluble in the bulk nor at CTB and CBP boundaries. In contrast to Mg, rare earth elements do not present good solubility at TBs in Ti. Solute atoms with smaller radius than Ti favor A-sites over B-sites at CTB and prismatic layer over basal layer at BP boundary, and solute atoms with larger radius than Ti favor B-sites over A-sites at CTB and basal layer over prismatic layer at BP boundary, being similar to the observations in Mg. We also computed the change in segregation energies of four solute atoms Ge, Zn, Y, Gd (two with smaller and two with larger metallic radius than Ti) as a function of normal strain at BP boundary, as shown in Figure 8b. We found that segregation energy decreases when the strain changes from compression to tension for the larger solute atoms (Ge, Zn) and increases for the smaller solute atoms (Y, Gd). The segregation of Y and Gd favors BP boundary over CTB if the tensile strain is larger than 2%. However, a large compressive strain may favor segregation of Ge and Zn to BP boundary over CTB, because of the large difference of segregation energies of these solutes at CTB and BP boundaries even in absence of any shear strain.

Solubility of 15 solute atoms in Zr is plotted in Fig. 9a and summarized in table V. Results for Zr are qualitatively similar as for Ti. Solute atoms with smaller radius than Zr favor A-sites at CTB and prismatic layer at BP boundary, and solute atoms with larger radius than Zr favor B-sites at CTB and basal layer at BP boundary, consistent with the observations in Mg and Ti. We also found, as for Ti, that most solute atoms smaller than Zr are soluble in bulk as well as TBs but most of the larger solute atoms are neither soluble in bulk nor at TBs. Segregation energies of four solute atoms Ge, Zn, Y, Gd as a function of normal strain at CBP boundary are shown in Figure 9b. Again, we found that segregation energy decreases with the normal strain change from compression to tension

for the larger solute atoms (Ge, Zn) and increases for the smaller solute atoms (Y, Gd). The segregation of Y and Gd, for tensile strain larger than 1%, favors CBP boundary over CTB boundary as shown in Fig 9b.

4.3 Remarks of solubility in hexagonal metals

Comparison of solubility of solute atoms in the bulk, CTB and BP/PB boundaries in Mg, Ti, and Zr shows that (a) solubility of most solute atoms is better at TBs than in the bulk; (b) Solute atoms with much larger or much smaller metallic radius than the matrix generally have a much better solubility at CTB and BP/PB even if they are not good soluble in bulk; (c) solubility of solute atoms is better at CTB than at CPB under zero normal strain at the boundary; (d) solubility at BP boundary linearly changes with normal strain at the boundary. Solubility improves for atoms with bigger metallic radius than the matrix when the normal strain changes from compression to tension. The reverse conclusions applies to solute atoms with a smaller metallic radius than the matrix; (e) for some solute atoms, the normal stress acting on BP boundary can change the relative solubility with respect to CTB.

Regarding solubility of 20 solute atoms in Mg, we found that (1) solute atoms, Ti, Zr, Na, Ba and K, are neither soluble in the bulk nor at CTB and BP/PB boundaries; (2) Solute atoms Al, Yb, Ce, La and Ca are energetically favorable at TBs but not in the bulk. Comparing solubility and segregation energy among all studied solute atoms in Mg, we can conclude that Al, Yb, Ce, La, Ca have a low solubility in the bulk but have good solubility at TBs. Solute atoms Ti, Zr, Na, Ba, and K are neither soluble in bulk nor at TBs. Regarding solubility of 14 solute atoms in Ti, we found only Ge, Zn, Al and In are soluble in bulk as well as at TBs. Other solute atoms that we doped in Ti are neither soluble in bulk nor at TBs, though solubility of most of solute atoms at TBs is better than in bulk. Ge and Zn are best candidates for doping in Ti with low segregation energy. Regarding solubility of 15 solute atoms in Zr, solute atoms, O, Ge, Zn, Al, Cd are soluble in bulk as well as at TBs. Oxygen has strong solubility in bulk as well as at TBs compared to other solute atoms, because of the formation of strong covalent bonds with Zr. The good solute candidates to dope in Zr are O, Ge, Zn, Al and Cd that have a smaller

metallic radius than Zr. Interestingly, a direct comparison of solubility in Mg and Zr (both have the same metallic radius ~ 0.16 nm) shows that the solubility of solute atoms is related to not only the atomic size but also other factors such as charge, local bonding and excess volume at TBs. For examples, the rare earth elements with metallic radius ~ 0.020 nm larger than Mg and Zr are good soluble at TBs in Mg but not in Zr.

5. Conclusion

Using DFT calculations, we studied $(10\bar{1}1)$, $(10\bar{1}2)$, and $(10\bar{1}3)$ CTBs and CBP/CPB boundaries in six hexagonal metals (Cd, Zn, Mg, Ti, Zr and Be), with focus on their structure and energy and solubility of solute atoms in these boundaries. The results can be summarized as follows:

- 1) The formation of twin boundary is associated with creation of excess volume. All studied metals have a positive excess volume associated with formation of $(10\bar{1}1)$ and $(10\bar{1}3)$ CTBs. However, the excess volume for the formation of $(10\bar{1}2)$ CTB is negative for Zr and Ti and positive for Cd, Zn and Be. For the CBP boundary, we found positive excess volume for Be and negative excess volume for Zn, Cd, and Zr.
- 2) $(10\bar{1}2)$ CTB has higher formation energy than $(10\bar{1}1)$ and $(10\bar{1}3)$ CTB for Mg, Ti, Zr and Be ($c/a < \sqrt{8/3}$), but lower for Cd and Zn ($c/a > \sqrt{8/3}$). $(10\bar{1}2)$ CTB has higher energy than CBP/CPB for all metals. This is consistent with the recent finding associated with pure-shuffle nucleation mechanism of a $(10\bar{1}2)$ twin, where a twin nucleus is primarily outlined by CBP/CPB boundaries instead of $(10\bar{1}2)$ CTB.
- 3) Solubility of solute atoms is in general better at TBs than in the bulk. Solute atom with much greater or much smaller metallic radius than the matrix generally has better solubility at TBs even if the solute is not soluble in the bulk.
- 4) Solubility of solute atoms varies linearly with normal strain at the BP boundary. Solubility of atoms with a bigger metallic radius than the matrix improves when the normal strain changes from compression to tension, but solubility of atoms with a smaller metallic radius than the matrix decreases when the normal strain changes from compression to tension.
- 5) Regarding solute selection in doping Mg, Ti and Zr, a good solute should be soluble

in bulk and better soluble in TBs. Thus, solute atoms such as Ge, Zn, Ce and La are good for doping Mg; solute atoms such as Ge, Zn Al and In are good for doping Ti; solute atoms such as Ge, Zn, Al, Cd are good for doping Zr. However, the effect of solute atoms on the mobility of CTBs and BP/PB boundaries still needs to be elucidated, and is a subject that we will pursue in future investigations.

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Figure 1. (a) A part of bulk hcp crystal (referred as matrix having 11 $(10\bar{1}2)$ planes). The circle and triangle represent the A and B planes along x-direction. (b) Atomic structure of the twin boundary that bonds the matrix and its mirror image with respect to the mirror plane M_1 (dashed line). d_0 is the interplanar spacing of $(10\bar{1}2)$ plane in the bulk. (c) Schematic of assembling the matrix and the mirror images into a bi-crystal with two identical twin boundaries. (d) The periodic bi-crystal model used in our simulations. The solid vertical lines show the periodicity of the simulation cell along y direction. The atoms at twin boundaries are shown in black.

Figure 2. (a) Atomic structure of $(10\bar{1}2)$ twin boundary with interplanar spacing $d_1 = d_0 + \delta$. d_0 is the interplanar spacing of $(10\bar{1}2)$ plane in the bulk. (b) Variation of the excess energy of the simulation cell as a function of δ for six metals. (c) The relaxed atomic structure near $(10\bar{1}2)$ twin boundary. (d) Variation of interplanar spacing of atomic planes near $(10\bar{1}2)$ twin boundary for Mg and Zr. The vertical lines indicate the interplanar spacing in the bulk.

Figure 3. Variation of excess energy of the simulation cell as a function of δ for six metals: (a) $(10\bar{1}1)$ twin boundary and (b) $(10\bar{1}3)$ twin boundary.

Figure 4. (a) Crystal orientations and unit cells of the basal-crystal and prismatic-crystal. (b) Atomic structure of a relaxed BP boundary for Mg. The thin vertical line indicates that the basal plane in the prismatic-crystal shifts towards the left with respect to the prismatic plane in the basal-crystal. (c) The excess energy of the simulation cell as a function of δ for six hexagonal metals.

Figure 5. The upper panels show relaxed atomic structure and charge density isosurface at $(10\bar{1}2)$ coherent twin boundary in Mg with and without solute atoms: (a) no solute atom, (b) a solute (Zn) at A site and (c) a solute (La) at B site. The A and B sites are marked in (a). The lower panels show relaxed atomic structure and charge density isosurface at coherent BP boundary in Mg with and without solute atoms: (d) no solute atom (e) a solute (Zn) in the prismatic layer and (f) a solute (La) in the basal layer. The top and bottom two atomic planes are fixed during relaxation.

Figure 6. (a) Solubility for solute atoms in bulk Mg and at A and B sites at $(10\bar{1}2)$ coherent twin boundary. (b) Solubility for solute atoms in bulk Mg and at coherent BP boundary. Solute concentration in both boundary planes is 25%.

Figure 7. (a) Schematic of normal stress at the BP/PB boundary under shear on coherent twin boundary. (b) Solute segregation at coherent BP boundary as a function of normal strain in Mg. Horizontal lines show solute segregation at coherent twin boundary (CTB) for the reference, and they are shown in the same color and line style as the segregation at coherent BP boundary.

Figure 8. (a) Comparison of solubility in Ti with respect to solute position in bulk, at $(10\bar{1}2)$ TB and BP boundaries. (b) Solute segregation at coherent BP boundary as a function of normal strain in Ti. Horizontal lines show solute segregation at coherent TB for the reference, and they are shown in the same color and line style as the segregation at coherent BP boundary.

Figure 9. (a) Comparison of solubility in Zr with respect to solute position in bulk, at $(10\bar{1}2)$ TB and BP boundaries. (b) Solute segregation at coherent BP boundary as a function of normal strain in Zr. Horizontal lines show solute segregation at coherent TB for the reference, and they are shown in the same color and line style as the segregation at coherent BP boundary.

TABLE I. Comparison of calculated lattice constants with the experimental lattice constants (shown in brackets) for six HCP metals. The lattice constants a and c are given in Angstrom. Experimental lattice constants are taken from Ref. (28).

Metal	a	c	c/a
Cd	3.038(2.98)	5.746 (5.62)	1.891 (1.886)
Zn	2.668 (2.67)	4.933 (4.95)	1.849 (1.856)
Mg	3.192 (3.21)	5.178 (5.21)	1.622 (1.623)
Zr	3.234 (3.23)	5.171 (5.15)	1.599 (1.593)
Ti	2.924 (2.95)	4.625 (4.68)	1.582 (1.587)
Be	2.263 (2.29)	3.571 (3.58)	1.578 (1.568)

TABLE II. A comparison of formation energies (mJ/m²) for $(10\bar{1}1)$, $(10\bar{1}2)$ and $(10\bar{1}3)$ CTBs and coherent BP boundary for six metals.

Metals	c/a	$(10\bar{1}1)$	$(10\bar{1}2)$	$(10\bar{1}3)$	BP
Cd	1.891	89.7	36.0	46.3	8.2
Zn	1.849	184.7	125.7	129.8	56.5
Mg	1.622	93.6	135.1	98.6	101.0
Zr	1.599	64.8	253.1	281.8	174.9
Ti	1.582	75.3	297.6	326.5	202.5
Be	1.578	404.6	632.2	455.7	534.7

TABLE III. The solubility (eV) in bulk, at A and B-sites at $(10\bar{1}2)$ twin boundary and in Basal and Prismatic layers at the BP boundary in Mg for solute atoms with metallic radius (Angstrom) bigger or smaller than Mg.

Solute	Metallic Radius	Solubility in bulk	Solubility at TB-A-sites	Solubility at TB-B-sites	Solubility at BP-Basal layer	Solubility at BP-Prism layer
Ge	1.25	-0.194	-0.357	0.012	-0.118	-0.327
Zn	1.34	-0.027	-0.209	0.159	0.015	-0.147
Ga	1.35	-0.254	-0.383	-0.081		
Al	1.43	0.091	-0.003	0.264	0.149	0.031
Ti	1.47	0.716	0.737	0.828	0.812	0.891
Cd	1.51	-0.267	-0.314	-0.138	-0.214	-0.303
Li	1.52	-0.231	-0.273	-0.132		
Zr	1.60	0.292	0.442	0.266	0.422	0.506
Sc	1.62	-0.068	0.097	-0.106	0.004	0.059
Yb	1.76	0.197	0.481	-0.060	0.113	0.239
Dy	1.78	-0.040	0.221	-0.277		
Y	1.80	-0.103	0.162	-0.337		
Gd	1.804	-0.062	0.209	-0.325	-0.088	0.050
Ce	1.82	0.036	0.331	-0.343	-0.019	0.139
Pm	1.834	-0.065	0.218	-0.376		
Na	1.86	0.353	0.495	0.287		
La	1.87	0.101	0.403	-0.310	0.019	0.184
Ca	1.97	0.070	0.351	-0.164	0.003	0.121
Ba	2.22	1.000	1.298	0.442		
K	2.27	1.447	1.746	1.089		

TABLE IV. The solubility (eV) in bulk, at A and B sites at $(10\bar{1}2)$ twin boundary and in Basal and Prismatic layers at the BP boundary in Ti for solute atoms with metallic radius (Angstrom) bigger or smaller than Ti.

Solute	Metallic Radius	Solubility in bulk	Solubility at TB-A-sites	Solubility at TB-B-sites	Solubility at BP-Basal layer	Solubility at BP-Prism layer
Ge	1.25	-1.402	-1.669	-1.262	-1.259	-1.454
Zn	1.34	-0.324	-0.535	-0.188	-0.121	-0.246
Al	1.43	-0.916	-0.967	-0.817	-0.797	-0.845
Cd	1.51	0.211	0.280	0.125	0.250	0.318
Mg	1.60	0.232	0.410	0.031	0.246	0.358
Sc	1.62	0.208	0.474	0.099	0.276	0.370
In	1.67	-0.240	-0.159	-0.337	-0.276	-0.198
Yb	1.76	1.660	1.940	1.490	1.648	1.774
Y	1.80	1.023	1.364	0.727	0.995	1.175
Gd	1.804	1.065	1.355	0.776	1.022	1.209
Ce	1.82	1.725	1.930	1.320	1.599	1.848
La	1.87	1.550	1.646	1.138	1.372	1.565
Ca	1.97	1.911	2.243	1.675	1.889	2.024
Sr	2.15	2.970	3.300	2.639	2.884	3.047

TABLE V. The solubility (eV) in bulk, at A and B sites at $(10\bar{1}2)$ twin boundary and in Basal and Prismatic layers at the BP boundary in Zr for solute atoms with metallic radius (Angstrom) bigger or smaller than Zr.

Solute	Metallic Radius	Solubility in bulk	Solubility at TB-A-sites	Solubility at TB-B-sites	Solubility at BP-Basal layer	Solubility at BP-Prism layer
O	0.60	-4.317	-4.770	-4.657	-3.946	-4.823
Ge	1.25	-1.125	-1.650	-0.939	-0.972	-1.386
Zn	1.34	-0.252	-0.708	-0.019	-0.091	-0.315
Al	1.43	-0.853	-1.140	-0.661	-0.713	-0.858
Ti	1.47	0.204	-0.009	0.356	0.299	0.188
Cd	1.51	-0.190	-0.336	-0.087	-0.007	-0.0717
Mg	1.60	0.049	0.007	0.159	0.251	0.245
Sc	1.62	-0.164	-0.050	-0.089	0.033	0.0273
Yb	1.76	0.798	1.025	0.794	0.893	0.985
Y	1.80	0.236	0.482	0.146	0.307	0.422
Gd	1.804	0.278	0.497	0.196	0.345	0.455
Ce	1.82	0.753	0.935	0.582	0.735	0.889
La	1.87	0.636	0.759	0.459	0.597	0.733
Ca	1.97	0.935	1.198	0.880	1.009	1.122
Sr	2.15	1.744	2.046	1.609	1.738	1.886