Basal-plane stacking-fault energies of Mg: A first-principles study of Li- and Al-alloying effects

J. Han, a X.M. Su, a Z.-H. Jin a,b,⇑ and Y.T. Zhu c

a School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
b State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China
c Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA

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Alloying effects due to Li and Al were examined in terms of generalized stacking-fault energies (GSFEs) associated with basal planes of hexagonal close-packed Mg. The GSFE profiles were obtained using a first-principles technique in combination with climbing-image nudged elastic band methods. Our results show that Li alloying can facilitate dislocation-mediated processes while sequential faulting across basal planes becomes favorable with Al alloying. Such a difference is attributed to the fact that the two alloying elements tend to form different types of bond critical points in Mg.

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Understanding the physical mechanisms associated with particular deformation modes helps in the development of materials with improved strength and ductility. Recently, introducing nanoscale twins within face-centered cubic (fcc) metals, such as copper, has been proved to be useful for obtaining stronger materials [1–3]. The strategy relies on, for example, the interaction mechanism between dislocations and twin boundaries [4–6]. It is therefore constructive to seek whether similar methodology can be extended to the materials of other structures, such as hexagonal close-packed (hcp) metals.

As prototypes of hcp metals, Mg and its alloys are potential engineering materials due to light weight and high specific stiffness [7]. However, the formability of such materials is quite limited because in hcp metals a sufficient number of independent slip systems are in general not readily available. For further development of this type of materials, how to control the microstructural morphology and microdefects so as to yield the best strength and ductility remains a fundamental concern.

A survey of the literature reveals that electrodeposited hcp Co may show high strength with sustained ductility, compared to most of other nanocrystalline metals reported so far [8]. Nanocrystalline Co processed by surface mechanical attrition treatment contains a high density of stacking faults on basal planes [9], which could be responsible for its exceptional mechanical performance. It is expected that a similar effect may also apply to Mg because the axial ratios of Mg and Co are nearly the same, i.e. c/a ~1.62, and in both metals the basal planes act as the primary slip system. For the purpose of design, it is necessary to understand various possible slip pathways associated with the basal planes in Mg and how alloying may affect such pathways.

We aimed to calculate the generalized stacking-fault energies (GSFEs) associated with basal-plane slip pathways in Mg. In particular, we focused on the so-called sequential faulting mechanism in hcp metals, a deformation process quite similar to mechanical twinning in fcc metals. We also attempted to check how alloying effects may disturb the GSFE surface after substitution with Li and Al atoms. Al is commonly used as an alloying element in Mg alloys to achieve better castability. Li may reduce the density and increase the ductility of Mg [7,10]. Although they may be considered as simple metals with nearly free electrons, in terms of charge or valence electrons, Al and Li are quite different alloying elements. It is interesting to see how the GSFE profiles are varied with alloying elements of different valency.

Here we propose a sequential faulting mechanism, which is essential to calculate the GSFE pathways at the basal planes. For hcp Mg, as a perfect dislocation slips on a basal plane, it dissociates into two partials...
with a fault ribbon formed in between, exactly the same as in fcc metals. However, this does not necessarily constitute the only possible way for basal-plane slip; it is easy to show that other possibilities also exist.

The sequential faulting mechanism involves a number of partial dislocations that occur in a successive manner. These partials are Shockley partials, and all slip one after another at successive basal planes, as illustrated in Figure 1. Let us start with any specified plane within a perfect hcp lattice, say L14, as marked in Figure 1a. An intrinsic I₁ fault can be formed by shearing the lattice above the specified plane such that a slip is generated with the Burgers vector $\alpha$ (Damiano notation [11]). We then repeat the process, starting with one plane above the specified plane, with the Burgers vector $\alpha C$, so that a T₂ structure will be generated. Repeating the process a third time, the same Burgers vector $\alpha C$ as in the first time can be used to generate an F₃ structure. This process, i.e. $\alpha \rightarrow \alpha C \rightarrow \alpha \rightarrow \cdots$, can continue as long as the lattice is displaced at a successive basal plane each time. F₃ can be viewed as consisting of a pair of intrinsic I₁ faults. Therefore, the consequence of the sequential faulting is to separate an I₂ into two I₃ through zigzag-type shifting on alternative (0001) layers. Further separation starting from F₃ involves merely a transformation from I₁ to I₀ (Fig. 1c). In this way, the sequential faulting is quite similar to the familiar deformation twinning process in fcc or bcc lattice.

To calculate the GSFE pathways associated with the sequential faulting mechanism, we constructed a slab model (Figs. 1a and 1b). The supercell is framed by $e_1 \times e_2 \times me_3$, with $e_1 = \frac{\sqrt{3}}{2}[1 \ 1 \ 2 \ 0]$, $e_2 = a_0[1 \ 1 \ 0 \ 0]$, $e_3 = c_0[0 \ 0 \ 0 \ 1]$ and $m = 17$, containing 30 (0 0 0 1) layers with 60 ions plus a four-layer vacuum gap to accommodate out-of-plane relaxations. I₂ is formed by shearing the 15th layer (L15) and above, T₂ by shearing L16 and above, and so forth. To study the pathway from I₁ to I₁', the supercell is constructed separately such that a fault I₁ $I'_1$ is introduced directly into the middle 15th (16th) layer. In the case of Mg-X (X = Li, Al) alloy, one Mg ion at the 15th layer is substituted by one X ion. On average, the model represents an alloy system of Mg-1.67 at.% X, where the concentration of X is well below the limiting solid solubility (~18 at.% for Li and ~12 at.% for Al).

The GSFEs were mapped out via density functional theory (DFT) calculations in combination with climbing-image nudged elastic band (CINEB) methods [12]. DFT calculations were performed with the Vienna Ab-initio Simulation Package (VASP) [13, 14]. The projector augmented wave method was used with core-valence electron interactions treated within the standard Blöchl scheme [15, 16]. The cutoff energy for plane wave basis sets was 287.854 eV. Brillouin zone sampling was performed using the Methfessel-Paxton smearing method with the width $\sigma = 0.2$ eV, and the k-points were meshed by $16 \times 18 \times 1$ Γ-centered grids. The CINEB method [17] was run with five images, and the quick-min optimizer was used to minimize all images along the band collectively with the forces less than 0.002 eV Å⁻¹. We also examined the GSFEs with the embedded atom method (EAM) potentials developed by Liu et al. [18] and Sun et al. [19] and the modified embedded atom method (MEAM) [20], for the sake of future molecular dynamics simulations.

The fully minimized GSFE curves involving three-layer slips are plotted in Figure 2. The stable and unstable fault energies determined from these curves are summarized in Table 1, together with literature data for comparison. The energies corresponding to I₂, T₂, F₃, I₁ and I₁' are denoted by $\gamma_{i2}$, $\gamma_{t2}$, $\gamma_{f3}$, $\gamma_{i1}$ and $\gamma_{i1}'$, respectively; the saddle points along the pathways define the unstable stacking-fault energies, i.e. $\gamma_{us}$ and $\gamma_{us}'$ as the lattice is faulted consecutively, the stable energies remain nearly unchanged and the barriers converge to the value of $\gamma_{us} + \gamma_{i1}$, similar to fcc metals [28]. The slight deviations between $\gamma_{i2}$, $\gamma_{t2}$ and $\gamma_{f3}$ may stem from the different local environment of the nearest planes according to the bond orientation model [26]. The most interesting result is that the addition of Li elevates the stable energies but hardly changes $\gamma_{us}$ and $\gamma_{us}'$; in contrast, the addition of Al drag down both $\gamma_{i2}$ and $\gamma_{us}'$.

Dislocation configurations depend on stable stacking-fault energies. Just considering an extended perfect

![Figure 1. The slab model and faulting pathway. (a) Front view and (b) top view of the model. The alloying element is denoted by a square. The cross-sections used in the analyses are labeled. (c) Schematic illustration of the sequential faulting mechanism. The red letters represent the separated fcc-like planes, where intrinsic I₁ faults occur. The Damiano notation [11] is shown at the lower right corner.](image)

![Figure 2. GSFE curves of Mg (triangle), Mg-Li alloy (square) and Mg-Al alloy (circle) along the pathways P–I₂–T₂–F₃ and I₁–I₁'.](image)
dislocation in a basal plane of Mg, the width of the stacking fault between the leading and trailing Shockley partials is inversely proportional to the stable fault energy, $\gamma_d$ [11]. With $\gamma_d(MgLi) > \gamma_d(Mg) > \gamma_d(MgAl)$, it is expected that the addition of Al tends to stabilize the extended dislocation configuration while Li tends to eliminate the separation such that other dislocation processes (e.g. cross-slip) might be favorable.

The GSFE pathways provide a critical measure for choosing plastic deformation mode most likely to occur [29–33]. If a leading partial dislocation is nucleated at a stress concentrator, whether the next nucleation event will generate a trailing partial on the same glide plane or a second leading partial on an adjacent plane will depend largely on the unstable fault energies along each path. In analogy to fcc metals [32], we may define two dimensionless parameters as characteristic material measures: $A_1 \equiv \gamma_d/\gamma_{us}$ and $A_2 \equiv (\gamma_{us} - \gamma_d)/(\gamma_{us} - \gamma_2)$. $A_1$ measures the probability that a trailing partial eliminates the stacking fault; $A_2$ is defined as the ratio of the energy barrier for sequential faulting over that for generating a trailing partial.

It simply follows that the sequential faulting is more likely to occur with decreasing $A_1$ or with $A_2 \rightarrow 1$. A rank may be obtained based on our GSFE data (Table 1), i.e. $A_1(MgLi) > A_1(Mg) > A_1(MgAl)$ and $A_2(MgLi) > A_2(Mg) \approx A_2(MgAl)$, suggesting that Al alloying is favorable to the deformation mode of sequential faulting, while Li alloying is favorable to dislocation-mediated slip. Of course, whether sequential faulting would actually occur also depends on the particular nucleation site and other factors, such as grain size.

The opposite trend revealed by the GSFE profiles due to Al- and Li alloying cannot be simply attributed to the atomic size effect, as both Al and Li atoms are smaller than Mg. Hence we have to explore the related electronic origins to elucidate the different alloying effects. The energy profile along a specified pathway is closely related to the charge flows induced by shearing [34,35]. The deviation of charge density may be analyzed using Bader’s theory [36] and the methods developed by Eberhart [37]. The topology of charge density can be characterized in terms of the so-called critical points (cps), the nodes with zero gradient of charge density functional in real space. The redistribution of charge density can then be viewed simply as the charge flow between cps [34].

Typical contour maps of charge density are illustrated in Fig. 3, which shows cross-section views of the fault planes marked as V01 and L15 in Figs. 1a and 1b, all intersecting with cps in Mg. For example, in the contour maps of V01, a cage critical point (ccp) appears at the octahedral interstice and a pseudo-atom (p-a) at one face of a tetrahedron (Fig. 3a). To produce a fault, say $I_2$, the charge redistributes mainly between L14 and L15, with little influence beyond the second nearest planes. The charge flow from p-a to ccp suggests the following pictures: in the unstable state ($US_1$), the octahedral and tetrahedral interstices are distorted, and an inter-layer bond critical point (bcp-I) (delocalized in [1120] direction) occurs within the doping layer to accommodate the structure change; when a fault is stabilized, the charge distribution resumes the original pattern, albeit the charge in L14 and L15 has spread out to some extent due to the lattice mismatch associated with the fault.

The charge distribution will be strongly perturbed as electrons scatter around the alloying element, and thus contribute to the change in GSFEs. Such energy change depends on the valency of the alloying element. With one less valence electron, Li depletes the electrons around itself, leading to the presence of an intra-layer bcp (bcp-II) between Mg pairs at L14 and L15 and a bcp-I within L15 (Fig. 3b). In contrast, with one more valence electron, Al enhances the charge density nearby so strongly that there is only one bcp-I confined in L15 (Fig. 3c). The bcp-I and bcp-II may respond to shearing in different ways. The bcp-I does not change too much during shearing, i.e. no significant charge redistribution is required – implying small resistance against shearing. A bcp-II instead has to be broken when deformed, making charge redistribution and readapting difficult – implying large resistance against shearing. With Li alloying the $\gamma_{us}$ presumably remains unaltered as a trade-off between two types of bcp, although the bcp-II reorientation may lead to an increase in $\gamma_2$. The situation with Al alloying is different. In this case, the formation of bcp-I dominates, so both $\gamma_{us}$ and $\gamma_2$ tend to be decreased, especially in the vicinity of the doping layer.

The alloying effects can be further examined by the local density of states (LDOS) associated with particular $s$- and $p$-bands (Fig. 4). Pure Mg has an almost featureless total DOS, corresponding to the behavior of nearly free electrons. The local disturbance of alloying elements to the host lattice yields excellent screening properties of electron gas, giving rise to a procrustean situation [38], as the Fermi level ($E_F$) must remain the same throughout the entire lattice. To satisfy the neutral charge condition, readapted valency bands are formed between the host ion and the alloying ion, evidenced by the appearance of a sunken shape for Li and a slight convex shape for the nearest Mg below $E_F$ (Fig. 4). As a result, Li ion weakens the bond at the doping site but makes the

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Table 1. Multi-basal-plane GSFEs calculated using CINEB-DFT methods and semi-empirical potentials (units in mJ m$^{-2}$).
surrounding Mg–Mg bonding stronger. In contrast, electrons are highly localized below $E_F$ in the case of Al, so the effect is opposite to that of Li. The bcps between Al pairs are enhanced by a larger fraction of localized electrons with reduced interaction strength between the neighboring Mg–Mg pairs. We also note that the $p$-band at the faulted plane is enhanced near $E_F$, indicative of reinforced bonding directionality. In Mg–Li alloy, the $p$-DOS of both Li and Mg increase, implying the existence of both bcps-I and -II. In Mg–Al alloy, however, only the $p$-band of Al is raised up substantially, while that of Mg is weakened slightly, indicating that with the aid of Al the bcp-I tends to dominate, in accordance with the analyses based on charge plots (Fig. 3).

In summary, according to the DFT-calculated GSFE profiles, the sequential faulting involving multiple basal planes constitutes a possible mode of plastic deformation in Mg or its alloys. Li alloying tends to increase the stacking-fault energies along the faulting pathways while Al alloying shows an opposite trend. Such a difference is highly relevant to the formation of two types of bcps, a chemical consequence of alloying elements with different valencies, instead of merely due to the atomic size effect.

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Figure 3. Contour maps of charge density from $P$, $US_1$ to $I_2$ in the cross-sections of V01 and L15 (see Fig. 1a and b). (a)–(c) The situations of Mg, Mg–Li alloy and Mg–Al alloy, respectively. The position of ccp is marked by a hollow circle, p-a by a solid circle, bcp-I by hollow arrows and bcp-II by solid arrows. For the initial state of Mg, the tetrahedral and octahedral frames are plotted.

Figure 4. LDOS of the atoms in the doping layer (L15) and its neighbor layer (L14) at initial state. The LDOS for (a) Mg–Li alloy; (b) Mg–Al alloy. The relevant $E_F$ is denoted by dashed lines.