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Intrinsic ductility of Mg-based binary alloys: A first-principles study

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{11−22}⟨11−23⟩ generalized stacking fault energies and {0001} surface energies of a wide range of Mg-based binary alloy systems were computed using first-principles methods. The intrinsic ductility of these systems was evaluated, taking into consideration the probability of dislocation emission and crack propagation. A design map based on the intrinsic ductility was constructed. The results provide a basis for the design of high-ductility Mg alloys.

Keywords: Magnesium alloys; Ductility; First-principles calculation; Stacking-fault energy

Due to their low specific density, Mg alloys have attracted considerable attention as a means for reducing vehicular weight. However, their poor plasticity and workability, which is attributed to pronounced basal slip during deformation, limit the use of Mg alloys in as-cast forms [1–4]. In recent years, the ⟨c+a⟩ slip system has been widely explored since it can provide five independent slip systems and can accommodate strain along ⟨0001⟩ direction, which is a critical requirement to achieve satisfactory ductility [5–8].

Intrinsically, materials are classified as ductile or brittle according to how they relieve concentrated stresses. In a brittle substance, the concentrated stress is relieved by the propagation of a pre-existing crack, producing two cleavage surface planes. In contrast to this, for a ductile material the concentrated stress at a crack tip is absorbed by the generation and motion of dislocations; as a consequence, the crack is blunted. Using a Peierls-type analysis, Rice [9] proposed a ductility parameter D to evaluate the intrinsic ductile vs. brittle behavior of materials under "Mode I" loading (tensile stress perpendicular to the cleavage plane) for cubic systems:

$$D = \frac{0.3\gamma_s}{\gamma_{us}} \quad (1)$$

where γ_s is the surface energy of two cleavage surfaces and equals the energy needed for the prorogation of a crack, and γ_{us} is the unstable stacking fault energy (SFE) which characterizes the resistance to the nucleation of a dislocation.

In face-centered cubic (fcc) systems, when the tensile load is set along the ⟨111⟩ direction, both the cleavage and slip plane are taken as {111}. Mehl and Papaconstantopoulos [10] calculated the ductility parameter of various fcc-structured metals (Ag, Al, Au, Cu, Ir, Pb, Pd, Pt and Rh). The results were in agreement with experimental observation that noble metals (Ag, Au and Cu) have excellent ductility. In detail, for Ag, Au and Cu, $D > 3$; for Pt, Pb and Al, $D \approx 1.5$; for Rh, Pd and Ir, $D \approx 1$. It should be noted that larger D means higher ductility.

For Mg with hexagonal-close-packed (hcp) structure, when the tensile load is set along the ⟨0001⟩ direction (perpendicular to the {0001} cleavage plane), the competition between the propagation of a pre-existing crack on the {0001} plane and the emission of a {11−22}⟨11−23⟩ dislocation determines its intrinsic ductility.

Furthermore, addition of alloying element(s) is known to effectively alter the surface energy and SFE of a system. Therefore, intrinsic ductility can be manipulated through selection of alloying elements. To this end, the effects of alloying on the intrinsic ductility of $MoSi_2$ were investigated by Du and Zhang [11], based on the computation of D values using a first-principles method. Their results revealed that the alloying element W decreases the D value from 1.08 to 0.90 for pure $MoSi_2$,

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while Nb, Tc and Ta increase the D value to 1.12, 1.16, 1.13, respectively. Accordingly, W embrittles $MoSi_2$ while Nb, Tc and Ta enhance the ductility, in agreement with experimental observations. However, a systematic study on the intrinsic ductility of Mg alloys has not been reported and current work only addresses the effects of alloying elements on SFEs [12–15], and essentially ignores their effects on surface energy. For the purpose of design, it is necessary and timely to gain a systematic understanding of how surface energy and SFE, and therefore the D value, vary with alloying elements in Mg.

In this study, the intrinsic ductility of a wide range of Mg-based binary alloys, including Ag, Al, Bi, Dy, Er, Ga, Gd, Ho, Li, Lu, Mn, Nd, Pb, Sc, Sm, Sn, Tl, Y, Yb, Zn and Zr, will be predicted using first-principles calculation. It should be noted the selected alloying elements have a maximum solubility of >1.0 at.%.

First-principles calculations were carried out using the Vienna Ab initio Simulation Package (VASP) [16,17], with the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form [18]. The cut-off energy was set as 400 eV. The Brillouin zone was sampled using a Monkhorst–Pack k-point mesh as follows: $4 \times 7 \times 3$ for the calculations of $\{11\bar{2}2\}\langle 11\bar{2}3\rangle$ generalized stacking fault energies (GSFEs) and $7 \times 8 \times 3$ for the calculations of $\{0001\}$ surface energies. First-order Methfessle–Paxton with smearing of 0.2 eV was used for structural relaxation until the total energy changes within 10^{-5} eV. The total energy calculation was then performed using linear tetrahedron method with Blöchl correction [19].

As illustrated in Figure 1a and b, supercells with 48 atoms were constructed in calculating the GSFE of the $\{11\bar{2}2\}\langle 11\bar{2}3\rangle$ slip system and surface energy of the $\{0001\}$ plane. For both cases, an atom in the sixth plane was substituted to simulate $Mg_{47}X_1$ systems. The slip process was simulated by gradually displacing the upper six layers with respect to the remaining six layers along $\boldsymbol{b}$ (Burgers vector). The GSFE is derived with the following equation:

$$\gamma_{GSFE} = (E_n - E_0)/A, \tag{2}$$

where E_n, $n \in (1,20)$, is the energy of the supercell with a displacement, E_0 is the energy of the original supercell, and A is the supercell's cross-sectional area.

Meanwhile, surface energy is calculated as follows:

$$\gamma_s = (E_{crack} - E_0)/A, \tag{3}$$

where E_{crack} is the energy of the supercell with a crack and E_0 is the energy of the bulk one, and A is the supercell's cross-sectional area. Note that in Eq. (1) γ_s is the energy of two surfaces, thus there is no "2" in the denominator of Eq. (3) though a crack-containing supercell has two surfaces.

In calculating the GSFEs, all atoms were allowed to relax along both the Z direction and the $[-1010]$ direction but were fixed in the slip direction, say $[-12-13]$. As listed in Table 1, for each of the alloys there are two unstable SFEs located at $0.3\boldsymbol{b}$ and $0.7\boldsymbol{b}$ and one stable SFE located at $0.5\boldsymbol{b}$. Our calculated SFE values for pure Mg, $0.3\boldsymbol{b}$ (242 mJ m^{-2}), $0.7\boldsymbol{b}$ (390 mJ m^{-2}) and $0.5\boldsymbol{b}$ (182 mJ m^{-2}), are lower than those reported by Wang et al. [14], which are $0.3\boldsymbol{b}$ (380 mJ m^{-2}), $0.7\boldsymbol{b}$ (463 mJ m^{-2}) and $0.5\boldsymbol{b}$ (221 mJ m^{-2}), respectively. This is because the calculated results are highly sensitive to the degrees of freedom adopted for the relaxation [20]. In brief, for the $\{11\bar{2}2\}\langle 11\bar{2}3\rangle$ slip system, the atoms on the two sides of the slip direction are unsymmetrical; as a consequence, there exists a force along $[-1010]$ during the slip process. In order to fully release this force, relaxation of all atoms along $[-1010]$ was performed in this work. In Wang et al.'s simulation, only two neighbor planes were allowed to relax along $[-1010]$, leading to higher SFE values compared with our results.

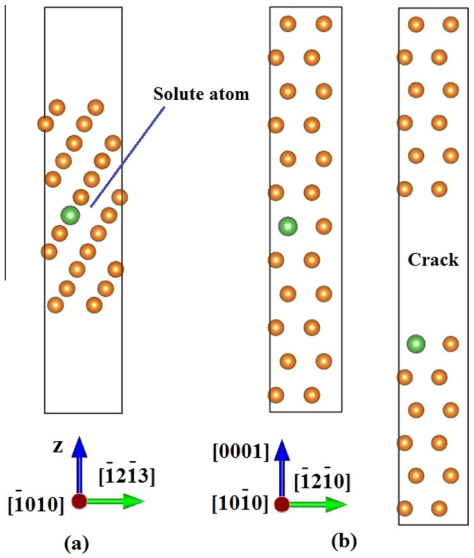

Figure 1. (a) Supercell used in the calculation of $\{11\bar{2}2\}\langle 11\bar{2}3\rangle$ SFEs. Z is perpendicular to both the $[-1010]$ and $[-12-13]$ directions; a vacuum width of 10 Å is added to avoid the interactions due to periodic images. (b) Supercell used in the calculation of $\{0001\}$ surface energies. The width of the crack is 20 Å. In both (a) and (b), one lattice site is substituted by a solute atom.

In predicting the surface energies, all atoms were fully relaxed in three dimensions. The calculated surface energy for pure Mg (1109 mJ m^{-2}) is in agreement with the published data of 1102 mJ m^{-2} [21]. The calculated GSFEs, surface energy and ductility parameter D for various Mg-based binary systems are listed in Table 1.

As shown in Table 1, the elements considered in this study can be ordered in terms of surface energy as follows: Bi < Pb < Yb ≈ Ca < Tl < Sn < (pure Mg) < Ga = Li < Zn < Al < Ag < Nd < Sm < Gd < Y < Dy < Ho < Er = Mn < Lu < Sc < Zr. Among these elements, Bi and Pb reduce the surface energy of Mg the most, decreasing it from 1109 mJ m^{-2} to 931 and 979 mJ m^{-2}, respectively; whilst Zr, Sc and Lu enhance the surface energy of Mg the most, increasing it from 1109 mJ m^{-2} to 1273, 1310 and 1485 mJ m^{-2}, respectively. Comparatively, Ga and Li leave the surface energy almost unchanged. Higher surface energy means more energy is needed for the propagation of a crack; however, this does not always result in a higher ductility, since there is another factor that should be taken into account, i.e. the nucleation of $\langle c+a\rangle$ dislocations.

In Mg alloys, $\langle c+a\rangle$ dislocation exists in a dissociated form, i.e. two ½ $\langle 11\bar{2}3\rangle$ partial dislocations with a $\{11\bar{2}2\}$ stacking fault in between [5,6]. The nucleation of a $\langle c+a\rangle$ dislocation is thought to proceed in three