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Alloying Mg with Gd and Y: Increasing both plasticity and strength

Lingling Tang [a], Wei Liu [a,*], Zhigang Ding [a], Dalong Zhang [c], Yonghao Zhao [a,*], Enrique J. Lavernia [c], Yuntian Zhu [a,b]

[a] Nano Structural Materials Center, School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
[b] Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA
[c] Engineering and Materials Science, University of California, Irvine, CA 92697-1000, USA

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ABSTRACT

The addition of rare elements to Mg enhances mechanical behavior via solution and precipitation strengthening mechanisms. To provide fundamental insight into the underlying mechanisms, we apply density-functional theory (DFT) calculations to systematically study the generalized planar fault energy (GPFE) for pure Mg and its alloys with Gd, Y, and Gd–Y. Special attention is focused on the $\{0001\}\langle 1\bar{1}00\rangle$ basal and $\{1\bar{1}00\}\langle 11\bar{2}0\rangle$ prismatic slip systems. Our results show that the addition of Gd and Y in Mg significantly reduces the magnitude of GPFE, in particular for the $\{1\bar{1}00\}\langle 11\bar{2}0\rangle$ prismatic slip system. The analysis of the charge density distribution reveals that the predicted reduction in GPFE can be primarily attributed to a decrease of shear resistance between the slip planes. Based on the criterion for the anisotropy of the dislocation mobility and disembrittlement parameter, we demonstrate that alloying Mg with Gd and Y yields lower resistance to slip and hence an improvement in plasticity. Our results also suggest that the strength and plasticity of the Mg–Gd–Y system can be simultaneously enhanced due to charge transfer between Mg and alloying atoms.

1. Introduction

The unique benefits of Magnesium (Mg) alloys, including: low density, ease of machinability, excellent damping capacity and favorable recyclability, render them an ideal material system for applications in the aerospace, aircraft and automotive industries, for example [1]. However, widespread utilization of Mg alloys has been hindered by their poor corrosion/creep resistance and low strength/ductility/plasticity. More recently, published studies suggest that the addition of rare elements to Mg can enhance the mechanical response as a result of solid solution strengthening and precipitation strengthening [2,3]. Studies on Mg–Gd-based alloys show, for example, that strength is influenced, not only by the amount of alloying elements, but also by the processing methodology (*e.g.*, incorporating plastic deformation), and by heat treatment [4–7]. In related work an strengthening effect was reported in an Mg–Gd binary alloy during compression testing and this was attributed to the pining effect of solute atoms on twin boundaries [7]. Moreover, it was reported that Mg–Y alloys have better plasticity than pure Mg because of the activation of additional slip modes [8,9]. In the case of ternary alloys, Mg–Gd–Y systems have been demonstrated to have high tensile yield strength, creep resistance, and corrosion resistance, due to the presence of metastable and stable precipitates that retain their stability at relatively elevated temperatures (up to 250 °C) [10–12]. A typical example of this behavior is provided by the extruded Mg–10Gd–3Y–0.6Zr in weight percentage (in wt.%) alloy [12], which has a ultimate tensile strength (UTS) of 462 MPa and yield strength of 382 MPa. These values are notably greater than those of most AZ series Mg alloys (UTS typically less than 300 MPa). Interestingly, however, and despite the fact that available published studies demonstrate that the strength of Mg can be significantly enhanced by alloying with Gd and Y, strategies to improve the plastic deformation of Mg and its alloys require additional research.

Density-functional theory (DFT) calculations have been widely accepted as a useful tool for understanding the mechanical behavior of metals. By calculating the generalized planar fault energy (GPFE), which indicates the energetic carried upon interrupting the normal stacking sequence of a crystal plane, DFT can predict dislocation core properties at the atomitic level; while at the macroscopic level, it can yield the stress intensity at which dislocations are nucleated at a crack tip [13]. Nowadays, investigation of GPFE in Mg alloys mainly focuses on different binary alloy systems, including Mg with Al, Ca, Cu, Zn, Fe, Mn, Li, Ni, Sn, Y, La, Gd, Nd and Zr [14,15]. In particular, Pei et al. [16] systematically studied GPFE

* Corresponding authors.
E-mail addresses: weiliu@njust.edu.cn (W. Liu), yhzhao@njust.edu.cn (Y. Zhao).

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profiles for five systems (*i.e.*, $\{0001\}\langle 11\bar{2}0\rangle$, $\{0001\}\langle 1\bar{1}00\rangle$, $\{10\bar{1}0\}\langle 11\bar{2}0\rangle$, $\{10\bar{1}1\}\langle 11\bar{2}0\rangle$ and $\{11\bar{2}2\}\langle 11\bar{2}3\rangle$) in Mg–Y alloys. Consistent with experimental results, DFT predicted that the addition of Y in Mg enhances the plasticity of Mg, resulting in an alteration in the dislocation core structure and lubrication of the dislocation motion [17,18]. As for Mg–Gd alloys, most theoretical studies have focused on the strengthening effect and stability of precipitated Mg–Gd precipitates, whist neglecting the influence of Gd on GPFE [19]. By using the generalized gradient approximation (GGA) method, Moitra et al. [20] revealed that the addition of Gd to Mg could increase the unstable stacking fault Υ_{usf} value of the $\{0001\}\langle 1\bar{1}00\rangle$ basal plane, but decrease the maximum GPFE value of $\{0001\}\langle 11\bar{2}0\rangle$ basal plane and $\{1\bar{1}00\}\langle 11\bar{2}0\rangle$ prismatic plane. In addition, GPFE investigations in ternary Mg alloy systems have been carried out for Mg–Zn–Y [21], Mg–Al–Zn [22], Mg–Al–Sn [23], and Mg–Zn–Ca [24]. However, GPFE curves of Mg with Gd and Y (Mg–Gd–Y) have not been extensively studied.

In view of the above discussion, in the present work, we study the GPFE curves for four Mg systems: Mg, Mg–6.4Gd, Mg–3.7Y, and Mg–6.2Gd–3.5Y (in wt.%) using DFT calculations, primarily focusing on the $\{0001\}\langle 1\bar{1}00\rangle$ and $\{1\bar{1}00\}\langle 11\bar{2}0\rangle$ slip systems. The $\{0001\}\langle 1\bar{1}00\rangle$ slip system represents the main deformation faults that form in the basal plane because as a result of the slip of partials, 1/3 $\langle 1\bar{1}00\rangle$, while among the prismatic or pyramidal plane slip systems, the $\{1\bar{1}00\}\langle 11\bar{2}0\rangle$ slip system is the easiest to be activated. Both systems are known to play an important role in affecting deformation mechanisms and mechanical properties. Considering that the spacing of (0001) plane is the largest for Mg and that fracture almost always occurs along the basal plane in Mg alloys, the surface energy of (0001) plane was calculated through first-principles rigid tensile tests. Note that the "fixed-grip" method is an universal and accurate approach to determine the surface energy or breaking strength in tensile test for most metal systems [25]. Based on the surface energy and results of GPFE, plasticity was evaluated by the anisotropy of the dislocation mobility and the disembrittlement parameter.

2. Calculation methods

DFT calculations were performed with the Vienna Abinitio Simulation Package (VASP) [26,27]. The Perdue–Burke–Ernzerh (PBE) version [28] was used as the exchange–correlation functional. The projector augmented wave (PAW) method [29] was used to treat interactions between ion cores and valance electrons. The cutoff energy for plane wave basis was set to 350 eV. The total energy accuracy was 5.0×10^{-5} eV atom^{-1}. Brillouin zone sampling was determined using a Gaussian smearing method with the width 0.1 eV and Monkhorst–Pack *k*-point mesh [27] as follows: $3 \times 3 \times 3$ for determining the location of Gd and Y atoms, $9 \times 9 \times 1$ for the GPFE of the $(0001)\langle 1\bar{1}00\rangle$ basal slip system. A *k*-point mesh of $9 \times 7 \times 1$ was used for determining the GPFE curves of the $\{1\bar{1}00\}\langle 11\bar{2}0\rangle$ prismatic slip system and for the first-principles rigid tensile tests. The convergence tests with respect to these parameters showed that the error bar for the total energy is less than 10 meV/atom.

A supercell consisting of 120 atoms was used to locate the Gd and Y atoms in Mg–Gd–Y model. As shown in Fig. 1a, an Mg atom was first substituted by a Gd atom (in red), and then a Y atom (in pink) was used to replace the nearest-neighbor and sub-nearest-neighbor Mg atom of Gd. We considered eleven possible positions for the substitutions, indicated as "Y1" to "Y11" in the figure. In all cases, the atomic positions were optimized with respect to all structural parameters until all Hellman–Feynman forces were less than 0.01 eV/Å. The cohesive energy, E_{coh}, was computed to determine the preferable site for Gd and Y atoms [30]:

$$E_{coh} = (E_{tot} - N_{Mg}E_{Mg} - N_{Gd}E_{Gd} - N_{Y}E_{Y})/(N_{Mg} + N_{Gd} + N_{Y})$$

where E_{tot} is the total energy of the entire system, E_{Mg}, E_{Gd}, and E_{Y} are the single Mg, Gd and Y atoms in an isolated state, respectively. N_{Mg}, N_{Gd}, and N_{Y} denote the number of Mg, Gd and Y atoms in the system, respectively. Our calculations showed that the Y9 site has the lowest cohesive energy and as such, a Y atom located at the Y9 site was used for the Mg–Gd–Y model all through this work. The models for calculating the GPFE of the basal slip system and prismatic slip system are illustrated in Fig. 1b and c, respectively. The supercell contains 12 metal layers with 96 atoms, and a 15 Å vacuum between periodically repeated slabs. Before calculating the GPFE, we compared the Υ_{usf} values to determine the location of Gd and Y atoms. Three positions were calculated: the Gd or Y atom was located in the first, second and third layers below the slip plane. As a result, both in the basal and prismatic slip systems, for Mg–Gd (Y) model, the slip plane was located between the layer containing Gd (Y) atom and the first layer above it (red atoms); in case of Mg–Gd–Y model, the slip plane was located just above the layer containing Y1 (blue atoms).

According to the Rice criterion, the plasticity can be evaluated by combining GPFE results with surface energy [31]. Upon determining GPFE curves, supercell with 96 atoms was performed on first-principles rigid tensile test to calculate the surface energy. There were 12 layers along the $\langle 0001\rangle$ direction, with a vacuum width of 15 Å to avoid image interactions between repeated slabs. The location of Gd and Y was determined in light of the lowest total energy of the considered system. In the Mg–Gd and Mg–Y models, three positions were calculated: the Gd or Y atom was located in the first, second and third layers below the separation plane. In the case of Mg–Gd–Y model, the mentioned three locations above were calculated; moreover, the separation plane that was located between the layers containing Gd and Y was also calculated. Consequently, as shown in Fig. 2a, for Mg–Gd (Y) model, the fracture plane is located between the first layer and the second layer above the layer containing Gd (Y) atom (red atoms); in the case of Mg–Gd–Y model, the location of fracture plane is the second layer above the layer containing Y atom and the third layer above the layer containing Gd atom (blue atoms). The surface energy was obtained by the difference of two total energies in the same system before and after deformation. As seen in Fig. 2b, the tensile deformation was realized through the introduction of 0.8 nm separation distances between two (0001) planes. During calculating, two atomic layers close to the upper and lower free surfaces of the cell were constrained while the calculations the rest atoms were allowed to fully relax.

3. Results and discussion

3.1. GPFE of the basal $\{000\}\langle 1\bar{1}00\rangle$ slip system

Fig. 3 shows the GPFE curves for the basal $\{0001\}\langle 1\bar{1}00\rangle$ slip system of the pure Mg, Mg–Y, Mg–Gd, and Mg–Gd–Y models. The calculated $\Upsilon_{usf}(basal)$ and $\Upsilon_{sf}(basal)$ values of pure Mg model (94 and 34 mJ m^{-2} respectively) are in good agreement with previous studies [32]. For Mg–Y and Mg–Gd models, $\Upsilon_{usf}(basal)$ values are determined to be 72 and 69 mJ m^{-2}, while $\Upsilon_{sf}(basal)$ values are 14 and 12 mJ m^{-2}, respectively. Compared with pure Mg model, the magnitude of $\Upsilon_{usf}(basal)$ for Gd and Y is decreased significantly by 26% and 23%, respectively. As for Mg–Gd–Y model, the $\Upsilon_{usf}(basal)$ and $\Upsilon_{sf}(basal)$ (84 and 21 mJ m^{-2} respectively) are lower than that of pure Mg model and higher than Mg–Y and Mg–Gd models. The $\Upsilon_{usf}(basal)$ value is decreased by 10% and thus presents