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First-principles study of solute–solute binding in magnesium alloys

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ABSTRACT

Solute–solute interactions play a major role in the properties of materials. In this work, we present an extensive database of solute–solute binding energies that captures the detailed interactions in Mg-based alloys from first-principles calculations based on density functional theory. The effects of solute–solute binding energies on magnesium properties, precipitation hardening responses and stacking fault energies in particular, are inferred and discussed. The results of our calculations regarding bindings between solutes with different chemistries, including Al–Sn, Al–Ca, Ca–Zn, Ca–In, and Sn–Zn, were validated using available experimental investigations. Solute pairs that were predicted to show large positive (e.g., Yb–Bi/Sn/Pb and Ca–Bi/Sn/Pb) and negative (e.g., Bi–Sn/Pb/Al) values of binding energies exhibited potential in modifying the precipitation sequence and stacking fault energy. Moreover, alloys added with these alloying elements may exhibit unique mechanical properties, which await experimental verification. Finally, the effect of physical features, including atomic radius and electronegativity, on the solute–solute bindings was investigated.

1. Introduction

Magnesium alloys in wrought forms (e.g., extrusions, forgings, sheet, and plates) have gained considerable worldwide interest in the past decade as potential replacements for heavier steel and aluminum alloys because of their high strength–density ratio [1–3]. However, the vast majority of Mg alloy applications are presently covered by cast products [1,4]. The application of wrought Mg alloys is hindered in part by their poor room temperature formability caused by their strong basal type texture and large anisotropy between basal and non-basal (prismatic and pyramidal) slips. The critical resolved shear stress of a basal slip system in Mg at room temperature is approximately two orders of magnitude lower than those of non-basal slip systems on prismatic and pyramidal planes and somewhat less than that of twinning. Therefore, basal slip and twinning are almost the only deformation mechanisms in polycrystalline Mg alloys at room temperature, which is far from the five independent operating systems required by the von Mises' criterion for sufficient ductility [5–8]. Meanwhile, the strength for most commercial Mg alloys is still substantially lower than their aluminum alloy counterparts, which is in part attributed to the low precipitation hardening responses of these alloys [3,9,10]. Therefore, developing new Mg alloys with higher strength and ductility is necessary for Mg alloys to remain competitive with aluminum alloys. In principle, the addition of alloying elements capable of modifying the precipitation sequence and the strengths of various deformation modes, thereby reducing crystallographic anisotropy, holds promise as a means to improve the strength and ductility of Mg alloys.

Over the past decades, numerous experimental studies on the influence of alloying additions on precipitation hardening responses of Mg alloys have been conducted [9–17]. The age-hardenability of Mg alloys improves significantly when the alloying elements for addition are selected appropriately. The interaction between solutes distinctly affects precipitation hardening responses by forming new types of precipitates or manipulating the density, distributions, sizes, morphologies, and growth orientation of the precipitates. For instance, the ultimate tensile stress of peak-aged Mg–6Gd–2Zn–0.6Zr (wt.%) alloys is nearly two times higher than its Mg–6Gd–0.6Zr (wt.%) counterpart because of the formation of the γ' ($Mg_{70}Gd_{15}Zn_{15}$, ordered hcp) phase [11]. Small additions of Zn in Mg-rare earth (RE) [11], Mg–Ca [12], and Mg–Sn [13] alloys have been widely reported to promote the formation of fine-scale precipitates and increase the precipitate number density during ageing heat treatment, thereby increasing the peak-aged hardness of alloys. Mendis et al. [14] observed that the number density of Mg_2Sn precipitates increased by

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approximately one order of magnitude in Mg–Sn alloys with the collective addition of Li + In, resulting in a hardening increment increase of ∼150%. Clustering or co-clustering of solute atoms has been proposed to possibly serve as heterogeneities for precipitate nucleation, leading to increased number density of the precipitates. The increased number density of thin prismatic plates in Mg–Ca alloys with added In has also been reported to enhance age-hardening response by three times [15]. It was suggested that the large strain field expected from Ca–In co-clusters changes the habit planes from basal to prismatic.

Alloying elements in the form of substitutional solutes also affect the strength and ductility of Mg alloys by modifying certain underlying factors, such as stacking fault energy and solute/dislocation interaction energy [5–7,18]. Stacking fault energy is directly associated with the dissociation behavior of dislocations, further affecting the strength, ductility, and fracture of materials. Nogaret et al. [19] correlated the dislocation structures and Peierls stresses to gamma surfaces (generalized stacking fault surfaces) in pure Mg. The simulation result, in which pyramidal I $\{1 0 -1 1\}\langle 1 1 -2 3\rangle$ slip efficiently occurs in comparison with the pyramidal II $\{1 1 -2 2\}\langle 1 1 -2 3\rangle$ slip, correlates well with the calculated gamma surfaces. Theoretical calculations of stacking fault energies of several binary Mg–X alloys have been reported in literature [20–23]. The effects of solutes on the basal [5,18], prismatic [6,7], and twinning dislocations [24] by inputting the first-principles data (e.g., size misfit, chemical misfit derived from stacking fault energy, and solute/dislocation interaction energy) into strengthening models have been quantitatively calculated in recent years. At present, investigating the multi-solute effects for Mg alloys is severely limited, although these effects have been recently reported for Al alloys [25]. However, the interaction between solute atoms plays an important role in stacking fault energy. For example, the unstable stacking fault energy of basal slip decreased more significantly for systems with simultaneous addition of Y and Zn than those with single Zn or Y additions [26]. The increased separation distance between two Shockley partial dislocations in Mg–Zn–Y alloys observed using transmission electron microscopy also demonstrates that the combined addition of Zn and Y leads to a significant reduction in stacking fault energy.

The interaction between solutes plays an important role in determining the underlying factors, such as precipitation process and stacking fault energy, further affecting the mechanical properties of Mg alloys. Binding energy, in terms of solute–solute/vacancy binding, captures the bonding properties of atoms and provides detailed information on the interaction between solute atoms. For the precipitation sequence, solutes with favorable bindings are likely to attract and form new types of precipitates, whereas those with unfavorable bindings tend to repel each other, thereby decreasing the solubility of solutes in the matrix and promoting precipitate density during aging treatments. For stacking fault energy, if two solutes with favorable binding are placed in two different basal planes, extra energy is definitely needed to shear crystals on this plane. Moreover, solute–solute binding energies can serve as input first-principles data to quantitatively predict the multi-solute effects for Mg alloys if a constitutive model is developed. Although solute-vacancy binding energies in Mg have been systematically studied by Shin and Wolverton [27] and Saal and Wolverton [28], calculation for solute–solute binding energies, at least to the best of our knowledge, only touches upon Al, Zn, Y, and Gd [29]. Therefore, it is necessary to take an extensive calculation of the binding energies of solute atoms in Mg to investigate the interaction between solute atoms.

In this paper, first-principles density functional calculations were carried out to calculate the binding energies of various solute pairs to construct an extensive first-principle database for predicting solute–solute binding energies in Mg alloy. Alloying elements with an equilibrium solid solubility larger than 0.5 (at.%) in Mg were selected: Ag, Al, Bi, Ca, Dy, Er, Ga, Gd, Ho, Li, Lu, In, Pb, Nd, Sc, Sm, Sn, Tm, Y, Yb, Zn, and Zr. The solute–solute binding energy trends were then investigated in terms of physical features, such as atomic radius difference and electronegativity difference of solute pairs. The charge density difference in selected planes of Mg–Bi–Yb and Mg–Bi–Sn alloys were computed to reveal the underlying mechanism of solute effects on the binding energies of solute atoms.

2. Computational details

In this study, first-principles total-energy DFT calculations were performed using the Vienna Ab-initio Simulation Package. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional for the generalized-gradient-approximation (GGA) and projector-augmented wave method was used in the present work [30–33]. All calculations were fully relaxed with respect to all degrees of freedom. The first-order Methfessel–Paxton with SIGMA = 0.2 eV was used for geometric relaxation until the electronic energy converged to less than 10^{-5} eV/cell and the Hellmann–Feynman force on all atomic sites was less than 0.01 eV Å^{-1}. Two successive structural optimizations (adapting basis vectors and computational grids to cell parameters) were conducted to ensure that the cell energies and structural parameters fully converged [34]. Total energy calculation was then performed using linear tetrahedron method with Blöchl correction [35,36]. A plane wave cutoff energy, which is 1.3 times the largest cutoff energy associated with the elements of interest recommended by VASP, was automatically performed by setting the PREC = HIGH in INCAR.

It is known that the *f* electrons are not handled well by presently available density functions because of their varying tendency to form localized states. A common solution to this problem is to place the *f* electrons in the core (so-called "frozen" potentials). The spatial localization of *f* electrons near the core is a good approximation and works well in Al–RE [37], Mg–RE [38], Mg–Pb, and Mg–Bi [7] alloys. Therefore, frozen potentials are used for energy calculation in systems embedded with *f* elements (RE, Pb, and Bi in the present work). Table 1 lists the PAW potentials and the corresponding cutoff energies for Mg and 22 solutes

Table 1
The PAW valence configuration, energy cutoff for the total energy calculation of pure Mg, Mg–X, and Mg–X–Z, and the atomic radius and electronegativity of Mg and the alloying elements considered in the present work.

Alloying element	PAWPP	Cutoff (eV)	Atomic radius (pm)	Electronegativity
Mg	[Ne]3s^{2}	164	160	1.31
Ag	[Kr]4d^{10}5s^{1}	325	144	1.93
Al	[Ne]3s^{2}3p^{1}	312	143.1	1.61
Bi	([Xe]4f^{14}5d^{10})6s^{2}6p^{3}	315	154.7	2.02
Ca	[Ar]4s^{2}	155	197	1
Dy	([Xe]4f^{10})6s^{2}	202	178.1	1.22
Er	([Xe]4f^{12})6s^{2}	201	176.1	1.24
Ga	([Ar]3d^{10})4s^{2}4p^{1}	175	135	1.81
Gd	([Xe]4f^{7})5d^{1}6s^{2}	201	180.4	1.2
Ho	([Xe]4f^{11})6s^{2}	200	176.2	1.23
In	([Kr]4d^{10})5s^{2}5p^{1}	125	167	1.78
Li	[He]2s^{1}	182	173.8	0.98
Lu	([Xe]4f^{14})5d^{1}6s^{2}	201	152	1.27
Nd	([Xe]4f^{4})6s^{2}	237	181.4	1.14
Pb	([Xe]4f^{14}5d^{10})6s^{2}6p^{2}	309	175	1.87
Sc	[Ar]3d^{2}4s^{1}	289	162	1.36
Sm	([Xe]4f^{6})6s^{2}	230	180.4	1.17
Sn	([Kr]4d^{10})5s^{2}5p^{2}	313	151	1.96
Tm	([Xe]4f^{13})6s^{2}	193	175.9	1.25
Y	[Kr]4d^{2}5s^{1}	263	180	1.22
Yb	([Xe]4f^{14})6s^{2}	146	193.3	1.1
Zn	[Ar] 3d^{10}4s^{2}	360	134	1.65
Zr	[Kr]4d^{3}5s^{1}	299	160	1.33