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Link between structural and mechanical stability of fcc- and bcc-based ordered Mg–Li alloys

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ABSTRACT

The first principles pseudopotential calculations based on the Perdew–Burke–Ernzerhof (PBE) form of generalized gradient approximation (GGA) within density functional theory (DFT) have been utilized to investigate the structural and elastic properties of cubic-based Mg–Li alloys. The heats of formation and elastic moduli were used in predicting structural stability profile, and their results are consistent with each other. In terms of phase stability, an interesting correlation between the calculated tetragonal shear modulus (C') and formation energy of corresponding bcc and fcc ordered compounds relative to hcp Mg and Li lattices is drawn. The predicted stability trend due to structural energy difference was further confirmed by electronic structure calculations based on Jones-type analysis.

1. Introduction

Magnesium is one of the readily available metals, constituting about 2.7% of earth's crust, offers several advantages including excellent machinability, recyclability, good castability, good weldability, good creep resistance, high thermal conductivity, and extreme lightness [1]. These features render magnesium alloys suitable and ideal for use in applications where lightweight to specific strength ratio is vital. At a density of 1.74 g/cm^3, magnesium (Mg) is amongst others the lightest structural metal. However, due to hexagonal close-packed (hcp) crystal structure, Mg and Mg alloys have undesirable mechanical properties at room temperature, including difficult workability. Fortunately, the addition of at least 11 weight percent (wt.%) lithium does not only reduce the density of magnesium but also transforms the hcp Mg into more workable body-centered cubic (bcc) phase [2]. The resulting magnesium–lithium (Mg–Li) alloys exhibit good formability and becomes the lightest metallic alloys with promising technological applications in transport (automotive and aerospace) and communication (portable electronic equipments) industries, due to their good strength-to-weight ratio and improved ductility. Furthermore, the existence of metastable fcc (face-centered cubic) at concentrations between 15 and 35 atomic percent (at.%) Mg has been predicted in the past, at least at very low temperatures [3].

Currently, the development of Mg alloys with desirable physical and mechanical properties with remarkable weight saving application remains a challenge. If the development of these alloys follows a path similar to Al alloys [4], using traditional trial and error methods and techniques, it would require a similar level of effort of many years. However, *ab initio* density functional theory (DFT) methods provide an opportunity to drastically accelerate materials research by efficiently predicting new phases and accurately describing their ground states [5]. Recently, *ab initio* calculations have concentrated on gaining a detailed knowledge of the electronic structure of materials and its effects on microscopic and macroscopic behaviours [6,7]. Considering these simulation advantages, the theoretical *ab initio* studies on Mg–Li system remain surprisingly scarce [8–10]. The work by Uesugi et al. focused only on hcp Mg$_7$Li alloy [8,9], while the more recent investigation by Counts et al. emphasized the mechanical properties of only bcc Mg–Li alloys using the supercell approach [10].

In this paper, the *ab initio* calculations based on pseudopotentials plane wave method were used to investigate existence of fcc and bcc binary Mg–Li alloys at 0 K for various concentrations, using ordered crystal structures. In order to avoid unworkable hcp Mg alloys, the current work attempts to find suitable alternative stable or metastable cubic low temperature formable Mg–Li alloys, from heats of formation. Furthermore, we investigate if these cubic

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phases possess desirable mechanical properties and are easily malleable. More recently, similar approach has been successfully used to study the phase stability [11] and mechanical properties [12] of other Mg-based binary alloys, and yielded results that are good agreement to experiments. The current work focuses on cubic Mg–Li ordered structures within 3:1 ($L1_2$ and DO_3) and 1:1 ($L1_0$ and B2) stoichiometries, while the end elements were taken as fcc and bcc for both Mg and Li. In order to study small additions of Mg and Li to pure Li and Mg metals respectively, we also examine the 7:1 and 15:1 stoichiometry in the fcc and bcc lattice, respectively. We will find which phases are more stable based on the predicted negative heats of formation and the structural formation difference (ΔH_f (bcc − fcc)). Furthermore, the mechanical stability for cubic crystals will be determined from tetragonal shear modulus, while elastic moduli and ratio of bulk to shear modulus (measure of ductility) will also be reported. Moreover, we will note the correlation on the trend of structural formation difference (ΔH_f (bcc − fcc)) and change in shear modulus ($\Delta C'$). In order to validate the phase stability in terms of structural energy differences, the electronic structure (ES) calculations due to electron band filling (electron per atom ratio) spanning the entire concentration range of fcc and bcc phases will be determined. ES was based on rigid-band model formalized by Jones-type analysis, and therefore provides composition ranges in which cubic phases are stable.

This paper is organized as follows, in Section. 2, the computational details followed to solve the electronic structure are briefly outlined. The trends in cohesive and elastic properties are respectively analysed and discussed in Section. 3. Finally, Section. 4 presents the conclusion of the paper.

2. Computational details

The equilibrium lattice parameters and electronic structure calculations were optimized using the *ab initio* plane wave (PW) pseudopotential method, embodied in the CASTEP code [13]. The Hohenberg–Kohn–Sham density functional theory (DFT) [14] was used within the GGA formalism [15] to describe the electronic exchange–correlation interactions. We used the recent PBE form of the GGA [16], which was designed to be more robust and accurate than the original GGA formulation. The Vanderbilt ultrasoft pseudopotentials [17] were employed for Mg–Li structures. Calculations were carried out on ordered fcc-based phases, $L1_2$ ($MgLi_3$, Mg_3Li, and ($MgLi_7$, Mg_7Li) and the bcc-based phases B2 (MgLi), B32 (MgLi), DO_3 ($MgLi_3$), Mg_3Li) and ($MgLi_{15}$, $Mg_{15}Li$). In addition, the structural energetics of tetragonal $L1_0$ (MgLi) and DO_{22} ($MgLi_3$, Mg_3Li) phases are reported. The first set of calculations were performed at our theoretically determined (equilibrium) lattice constants for each structure [18], with a plane wave basis set defined by an energy cut-off of 500 eV for all considered superstructures. Furthermore, the minimum and maximum Guassian smearing width were respectively set at 0.4 and 0.1 eV for superstructures, and at 0.1 and 0.01 eV for elemental metals, since the lattices of the latter involve energy differences of the order 1–100 meV/atom than is required in the former. In addition, this condition requires the use of denser Monkhorst–Pack [19] sets of **k**-points and a little alteration to the defaulted setting within the code, especially in case of Li, than it is averagely and adequately acceptable, respectively, for Mg and alloyed compounds. These parameters are essential since the Fermi energy, and hence the total energy depends quite sensitively on them. The convergence criterion of less than 2×10^{-5} eV on total energy per atom, 10^{-3} Ǻ on the displacement of atoms, 0.05 eV/Ǻ on the residual forces, and 0.1 GPa on the residual bulk stress was used. Uncommonly, a special care was taken when treating Li element, only during structure relaxations to avoid emanating stable phase disagreements with experiments. With our choice of mesh grid in the full Brillouin zone, the selected sufficient cut-off energy and **k**-points were converged to within 1 meV/atom and 5 meV/atom for pure elements and superstructures, respectively.

The second set of calculations was performed to obtain elastic coefficients of Mg–Li alloys using CASTEP on Materials Studio version 3.0 interface [20]. We used six different values of the strain ±0.0008, ±0.0024 and ±0.004 for each structure. The application of strain on the lattice implies a lowering of symmetry from that of the crystal, therefore very accurate total energy calculations are required, since the energy differences involved are of the order 10–1000 μeV/atom. In addition, this condition requires the use of slightly denser **k**-points to be utilized than in geometry optimization of crystals. The current set of calculations was considered converged when the maximum force on atoms was below 0.01 eV/Ǻ, the total energy change per atom was less than 4×10^{-4} eV/atom and the displacement of atoms was below 4×10^{-4} Ǻ. The value of the stress was automatically computed for each strain, and resulted in a stress–strain linear fit curve, from which each component of the stress was computed, and respective gradients provided the values of the corresponding elastic constants. Based on three independent single crystal elastic constants of a cubic crystal, C_{11}, C_{12}, C_{44} the elastic moduli of polycrystalline material were calculated following averaging schemes of Voigt (upper bound) and Reuss (lower bound) as follows [21]:

$$E = \frac{9BG}{3B+G}, \quad G = \frac{1}{2}\left[\frac{C_{11}-C_{12}+3C_{44}}{5} + \frac{5C_{44}(C_{11}-C_{12})}{4C_{44}+3(C_{11}-C_{12})}\right]$$

$$B = \left(\frac{C_{11}+2C_{12}}{3}\right), \quad C' = \frac{C_{11}-C_{12}}{2}, \quad A = \frac{(2C_{44}+C_{12})}{C_{11}}$$

where E is the Young's modulus, G shear modulus, B bulk modulus, C' tetragonal shear modulus and anisotropic factor A.

3. Results and discussions

3.1. Structural stability

The equilibrium lattice parameters, a_0, of the geometrically optimized structures are listed in Table 1. In calculations where the ordered superstructures were used, resulting to twice the value of a_0, the calculated a_0 values listed in Table 1 were normalized, for comparison purposes. With increasing Li concentration, the lattice parameter decreased to its minimum at 50:50 equi-atomic compositions, after which a slight increase in a_0 is observed. The observed trend, which deviates slightly from Vegard's law for solid solutions, is similar in both bcc and fcc Mg–Li alloys considered in this study. This behaviour was also realised in earlier theoretical [3,22] as well as experimental [23,24] studies. Although the lattice parameter of bcc Li is underestimated by current and other calculations [25,26], in general our predicted lattice parameters are in good agreement with available experimental and theoretical results.

The heat of formation, H_f, of the alloy is computed according to the relation [11,25]

$$H_f^{Mg_{1-x}Li_x} = \frac{1}{n}E_{total}^{Mg_{1-x}Li_x} - \left[(1-x)E_{solid}^{Mg} + xE_{solid}^{Li}\right] \qquad (1)$$

where $E_{total}^{Mg_{1-x}Li_x}$ is the total energy of the alloy, E_{solid}^{Mg} and E_{solid}^{Li} are the total energies of the stable structures of elemental Mg and Li, n is the total number of atoms in the superstructure, x and $(1-x)$ refer to the fractional concentrations of the constituent elements.

We note that the heat of formation curve shown in Fig. 1 makes a V-shape, with its minimum at the equi-atomic concentration of Mg–Li compound. At 50–50 concentration, the B2 structure is