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First-principles simulations of plasticity in body-centered-cubic magnesium–lithium alloys

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Abstract

First-principles quantum mechanics is an increasingly important tool for predicting material properties when designing novel alloys with optimized mechanical properties. In this study, we employ first-principles orbital-free density functional theory (OFDFT) to study plastic properties of body-centered-cubic (bcc) Mg–Li alloys as potential lightweight metals for use in, e.g., vehicle applications. The accuracy of the method as a predictive tool is benchmarked against the more accurate Kohn–Sham DFT (KSDFT). With a new analytic local electron–ion pseudopotential, OFDFT is shown to be comparable in accuracy to KSDFT with the conventional non-local pseudopotential for many properties of Mg–Li alloys, including lattice parameters and energy differences between phases. After this validation, we calculate generalized stacking fault energies (SFEs) of a perfect lattice and Peierls stresses (σ_p's) for dislocation motion in various bcc Mg–Li alloys. Such predictions have not been made previously with any level of theory. Based on analysis of SFE barriers, we propose that alloys with 31–50 at.% Li will exhibit the greatest strength. Their σ_p's are predicted to be 0.18–0.31 GPa. The Li concentration in this range (31–50 at.%) has little impact on plastic properties of bcc Mg–Li alloys, while atomic-level disorder may decrease the σ_p. This range of σ_p is similar to the industrial goal for potential lightweight Mg alloys.

Keywords: Magnesium alloy; Stacking-fault energy; Peierls stress; Density functional theory; Atomistic simulation

1. Introduction

Development of lightweight metal alloys with optimized mechanical properties would provide enormous benefits for fuel-efficient vehicles. There has been a surge of interest in the use of magnesium (Mg) as a lightweight structural material because of its low density (1.74 g cm^{-3}), excellent specific strength and dent resistance, and ample availability [1–4]. The automobile industry has provided a major driving force for Mg applications, since the demand for lightweight construction materials is increasing in order to improve vehicle fuel efficiency in a world of decreasing fossil fuel supplies. Although Mg and its alloys are already found in current automobiles, e.g., engine cradles, steering columns, instrument panels and gearboxes [1,5], there is less than 1 wt.% use in the average vehicle [6,7]. Mg's hexagonal-close-packed (hcp) crystal structure leads to limited ductility and toughness, which severely constrains the application of standard metal-forming techniques [1–3]; therefore, many challenges exist to introducing Mg into various car components.

Mg's low formability is mainly due to a large anisotropy between slip systems. For instance, the critical resolved shear stress (CRSS) on the basal slip plane is ~0.5 MPa [8,9], which is much smaller than those on the next lowest energy slip planes, such as 39.2 MPa (prismatic) [10] and 105 MPa (pyramidal) [11]. One way to make Mg more formable is to convert its crystal structure from brittle hcp to ductile face-centered-cubic (fcc) or body-centered-cubic (bcc),

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which activates more than five slip systems near room temperature, as required by the von Mises criterion [12]. Alloying with lithium (Li) is of particular interest. Above ~17 at.% Li (5.5 wt.%), the hcp Mg–Li alloy becomes a duplex alloy with both hcp and bcc phases present simultaneously; above ~31 at.% Li (11.5 wt.%), the alloy is entirely bcc [13]. The brittle-to-ductile transition coupled with Li's even lower density (0.58 g cm^{-3}) suggest substantial benefits of using Mg–Li alloys for further weight saving.

Plastic deformation mechanisms, mainly governed by dislocation motion, are not well studied in Mg–Li alloys. These mechanisms are difficult to explore experimentally, because the synthesis of alloys with specific atomic compositions and structures can be tricky or essentially impossible. Moreover, no in situ, real time experimental methods exist to directly characterize both atomic scale features and their subsequent behavior upon mechanical deformation. This situation presents an opportunity for computational methods to provide predictions of mechanical properties of Mg–Li alloys as a function of atomic configurations and their local structures, which can then be used to aid the design of novel lightweight alloy materials.

Among computational techniques, the classical embedded atom method (EAM) [14,15] has been ubiquitously used to investigate mechanical properties of many metallic systems; however, it is most easily applied to pure metals. Alloy potentials require additional fitting for functions representing the cross-interaction for different elements. This requirement has greatly limited the extension of such methods to complex alloys. Therefore, a reasonably accurate interatomic potential dealing with both hcp and bcc Mg–Li binary alloys simultaneously was not developed until 2012 [16]. This state-of-the-art Mg–Li potential is constructed based on the second-nearest-neighbor modified EAM; it reproduced quite well static bulk properties of Mg–Li alloys, e.g., lattice parameter, bulk modulus and phase ordering [16]. However, no predictions of plastic properties of bcc Mg–Li alloys, e.g., generalized stacking fault energies (SFEs) and dislocation motion, have been made as yet using this potential. We have shown [17,18] that the most accurate EAM potential available for Mg [19] leads to, e.g., spurious cross-slip of dislocations between basal and pyramidal slip planes, and other problems that lead us to question the reliability of such potentials for plasticity predictions. Therefore, more validation tests would need to be made in order to reliably use this new Mg–Li EAM potential to reliably investigate deformation properties of Mg–Li alloys.

In principle, a superior alternative to the EAM would be a first-principles quantum mechanics (QM) method, which would provide a predictive, non-empirical approach for studying metal properties without additional overhead when treating multi-component alloys. However, conventional QM calculations are too demanding to explicitly simulate dislocations in metals, which typically requires the explicit treatment of thousands of atoms; successful QM studies on Mg–Li alloys have thus far been limited to calculations using less than 100 atoms, e.g., calculating elastic constants [20] or searching for equilibrium structures [21].

In this work, we use an efficient first-principles QM method called orbital-free density functional theory (OFDFT) [22]. Unlike conventional Kohn–Sham DFT (KSDFT) [23,24] that uses single-electron orbitals to evaluate the non-interacting electron kinetic energy, OFDFT solves directly for the electron density as the sole variable. Without the need to construct orthogonal orbitals, implementations of OFDFT terms can be made nearly linear scaling with system size ($NlnN$) with a small prefactor. With this scaling, one can explicitly calculate 10^3–10^6-atoms with QM accuracy at moderate computational cost [25]. Two approximations within OFDFT, namely a kinetic energy density functional (KEDF) and a local electron–ion pseudopotential (LPS), have proven to be reliable for describing fundamental mechanical properties of main group metals with an accuracy comparable to KSDFT [17,26–31]. OFDFT has been successfully deployed in a number of large-scale QM simulations, e.g., liquid metals [27,32,33], void growth [34], nanowire deformations [35,36], crack tip behavior [31], grain boundary migration [37] and dislocation behavior [17,18,30,38]. Of particular note is that OFDFT quasistatic loading simulations are able to reproduce remarkably well the measured Mg CRSSs for the basal and non-basal (prismatic) slip systems [18]. These results lend credence to OFDFT as an independent, predictive tool for simulating plastic behavior of main group metal alloys with first-principles accuracy.

In order to simulate deformation properties as a function of atomic composition, we model various ordered $2 \times 2 \times 2$ bcc Mg–Li supercells containing two atoms in each unit cell, for a total of 16 atoms in each supercell. In order to examine how local structure affects material plasticity, we also model a less-ordered, quasirandom bcc structure for comparison. This less-ordered structure is obtained based on the special quasirandom structure (SQS) method [39–41], which is designed to mimic local pair and multisite correlation functions of the random alloy with smaller numbers of atoms in a periodic unit cell.

In the present work, we begin by benchmarking our OFDFT model against KSDFT (properties used as benchmarks given in parentheses) for: (1) pure Li (bcc Li lattice parameter, bulk modulus, elastic constants and unstable SFE (γ_{us}, energy barrier to slip) along a <1 1 1>{1 1 0} slip system, and energy differences between various bulk phases); (2) MgLi (B2 (CsCl-type) MgLi alloy formation energy (ΔE_f), lattice parameter, bulk modulus, elastic constants and γ_{us} along a <1 1 1>{1 1 0} slip, and the energy difference between B2 and B32 (NaCl-type) phases (ΔE_{B32-B2})); and (3) various $2 \times 2 \times 2$ Mg–Li alloys (bcc lattice parameter and energy differences between hcp and bcc ($\Delta E_{hcp-bcc}$)). These wide-ranging benchmark metrics cover equilibrium to plastically deformed states in pure Li and Mg–Li alloys. Note that extensive benchmarking of the OFDFT model was already reported for pure hcp

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