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Thermodynamic stability of Mg–Y–Zn long-period stacking ordered structures

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Although long-period stacking ordered (LPSO) structures have been known to improve mechanical strength in Mg alloys for over a decade, only recently have LPSO crystal structure models been proposed. Using density functional theory (DFT), we explore the thermodynamic stability of two such models with Mg–Y–Zn LPSO structures of 18R and 14H types. All LPSO structures are predicted to be metastable when compared to the 0 K ground state phase diagram, which we construct from DFT calculations of 13 Mg–Y–Zn intermetallic compounds.

Keywords: Magnesium alloys; LPSO; Phase stability; Density functional theory; Phase diagram

Although there is growing interest in magnesium alloys as a lightweight alternative to aluminum-based alloys in transportation applications, poor strength and ductility remain key issues to be resolved. Rare-earth alloying is a promising method to improve Mg alloy strength, and large increases in strength have been observed in extruded Mg–Y–Zn and other similar alloys with small solute addition (as low as 3 at.%) without sacrificing ductility. Such high-strength Mg-rare earth alloys were first reported in 2001 for $Mg_{97}Y_2Zn$, with a tensile yield strength of 610 MPa at 5% strain [1]. This increase in strength is attributed to crystallographically peculiar precipitates known as long-period stacking ordered (LPSO) structures [2], consisting of ordered hexagonal close-packed (hcp)/face-centered cubic (fcc) stacking sequences [3,4]. LPSO structures are classified by the period of the plane stacking ordering and whether the stacking produces hexagonal (H) or rhombohedral (R) symmetry. They primarily exhibit 14H and 18R symmetry, with 18R transforming to 14H with annealing [5].

The thermodynamic stability of LPSO structures remains questionable. It has been suggested that 14H LPSO precipitates are a thermodynamically stable ternary phase, as they remain after aging at 773 K [4,5]. Indeed, a so-called “X-phase” was reported in the Mg–Y–Zn system of $Mg_{12}YZn$ composition [6] and has since been revealed to be an 18R LPSO [7,8]. A key test of stability is the ability to synthesize and equilibrate the LPSO structure as a single phase. However, to the best of our knowledge, isolated LPSO single-phase samples have not been reported, although a 95% volume fraction of LPSO phase (with $Mg_{24}Y_5$) has recently been observed [3].

Density functional theory (DFT) has proven to be an effective tool for investigating precipitate stability in Mg and other alloy systems [9–15]. There have been only two previous DFT investigations in LPSO phase stability, both reporting negative formation energies with respect to the elements of simplified 6H LPSO structures [16,17]. A negative formation energy is a necessary but not sufficient condition for LPSO phase thermodynamic stability, merely indicating stability with respect to decomposition into the pure elements. There are many examples of phases which have negative formation energies yet are metastable with respect to the set of stable phases (the so-called convex hull) [10,18,19]. Indeed, as will be discussed shortly, the 18R structure, which transforms to 14H after annealing [5], has a negative formation energy yet is metastable with respect to 14H. For an LPSO structure to be a thermodynamically stable 0 K ground state, it must be lower in energy than any combination of phases in the Mg–Y–Zn ternary system.

To investigate whether 14H and 18R Mg–Y–Zn LPSO structures are thermodynamically stable, we first construct the 0 K Mg–Y–Zn ternary ground state phase

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diagram from the DFT predicted formation energies of the binary and ternary compounds in the Mg–Y–Zn ternary system. Then we compare the convex hull formation energies to the formation energies of two experimentally derived Mg–Y–Zn LPSO structure models [3,4].

Two crystallographically resolved structure models for 14H and 18R LPSO structures have been proposed [3,4] and both are employed in the current work. They consist of hcp-stacked unary Mg layers sandwiched in between pairs of fcc-stacked ternary (Mg_2YZn) chemically ordered layers. One model has a sharp change from unary to ternary layers across the fcc/hcp transition [4] whereas in the other model the transition is more gradual, introducing an intermediate Mg–Y binary layer [3]. The models also differ in the decoration of Mg, Y and Zn in the ordered Mg_2YZn layers. These two structure models are referred to as the sharp and gradual models in the remainder of the paper. Within each model, the only difference between 14H and 18R structures is the quantity of hcp Mg unary layers: 14H contains five and 18R contains four in the sharp model (three and two in the gradual model, respectively).

First-principles calculations are performed with DFT as implemented in the Vienna Ab-initio Simulation Package (VASP) [20,21]. The electron exchange and correlation are described with the generalized gradient approximation of Perdew, Burke and Ernzerhof [22], using the potentials supplied by VASP with the projected augmented wave method [23]. The electronic and crystallographic ground states of all the structures in the current work were determined by relaxing all degrees of freedom, reducing atomic forces to under 0.01 eV $Å^{-1}$. Relaxation of the LPSO crystal structures began at their measured atomic positions and lattice parameters [3,4]. The total energy of the structures were converged to within 1 meV $atom^{-1}$ using an energy cutoff of 276 eV and gamma-centered k-point meshes of approximately 6000 k-points per reciprocal atom density. The formation energy (per atom) with respect to the elements, ΔH_f, of a $Mg_xY_yZn_z$ compound is calculated by:

$$\begin{aligned}\Delta H_f(Mg_xY_yZn_z) = {} & E(Mg_xY_yZn_z) \\ & - \frac{x}{x+y+z}E(Mg) \\ & - \frac{y}{x+y+z}E(Y) \\ & - \frac{z}{x+y+z}E(Zn) \qquad (1)\end{aligned}$$

where $E(i)$ is the DFT total energy per atom of structure i. We define the stability of an LPSO structure, ΔH_{stab}, as the energy of the LPSO structure with respect to the energy of the convex hull at the LPSO structure's composition, $E_{CH}(Mg_xY_yZn_z)$:

$$\begin{aligned}\Delta H_{stab}(Mg_xY_yZn_z) = {} & E(Mg_xY_yZn_z) \\ & - E_{CH}(Mg_xY_yZn_z) \qquad (2)\end{aligned}$$

If ΔH_{stab} is zero, then the LPSO structure lies on the convex hull and is thermodynamically stable. If ΔH_{stab} is positive, then the LPSO structure lies above the hull and is metastable. The set of phases that comprise the convex hull at a given composition is determined by comparing all possible sets of phases, with canonical linear programming [24], to find the set with lowest energy.

Mg–Y–Zn 14H and 18R LPSO structures of both the sharp and gradual models have been calculated with DFT, including two 18R gradual structural models in which the stacking of the sets of binary and ternary fcc layers differ, resulting in monoclinic and trigonal space group symmetries [3]. The DFT predicted lattice parameters for all five LPSO structures are compared to experiments in Table 1. The predicted lattice parameters show good agreement with experiments, with larger differences for the two sharp model LPSO structures.

Predicting the thermodynamic stability of the LPSO structures requires calculating the energies of the other phases in the Mg–Y–Zn ternary system with which the LPSO structures must compete. Therefore, all unique binary and ternary compounds in the Mg–Y–Zn system from the International Crystal Structure Database (ICSD) with primitive cells of less than 60 atoms and without partial site occupancy were calculated by DFT (13 in total). Their formation energies are listed in Table 2. Five ternary compounds are present in the experimentally derived Mg–Y–Zn phase diagram [25] (W-$Mg_3Y_2Zn_3$, Z-$Mg_{28}Y_7Zn_{65}$, I-Mg_3YZn_6, H-$Mg_{15}Y_{15}Zn_{70}$, X-$Mg_{12}YZn$). However, their crystal structures are not found in the ICSD. Instead, two other stoichiometric ternary Mg–Y–Zn compounds are present in the database, one of which, $Mg_{18}Y_9Zn_{58}$, is prohibitively large for DFT, with 680 atoms in the primitive cell. Consequently, only one ternary compound is included in the current study of LPSO stability, MgYZn [26]. Note that, since ternary compounds not presently considered are expected to be more stable than MgYZn at the LPSO structure compositions, the current prediction for $E_{CH}(Mg_x Y_yZn_z)$ may be underestimated. Consequently, the stabilities of the LPSO structures, according to Eq. (2), are overestimated in the current work. In other words, the LPSO structures are likely to be less stable than currently predicted.

The 0 K ternary phase diagram is determined from the DFT prediction of the formation energies of the 13 Mg–Y–Zn compounds, as shown in Figure 1. At compositions for the LPSO sharp model, Mg and MgYZn are stable (they are said to lie on the system's convex hull). For the gradual model, Mg and MgYZn are stable along with $Mg_{24}Y_5$, due to the 4:3 Y:Zn ratio in the gradual model structures. $Mg_{24}Y_5$ has been observed alongside LPSO structures [3,8,27].

The formation energies and stabilities of the LPSO structures are given in Table 3. Although all the LPSO structures have a negative formation energy with respect to the elements, they are not stable with respect to the convex hull at 0 K. The gradual LPSO structures are metastable by only about 10 meV $atom^{-1}$, a reasonably small amount of energy which allows the possibility that the structures are stabilized at elevated temperatures by entropy (vibrational, electronic and configurational) at the temperatures at which they are observed. Furthermore, 10 meV $atom^{-1}$ may lie within the error of DFT formation energies, which can be estimated in the current work from the binary experimental values in Ta-