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# The phase stability and elastic properties of $MgZn_2$ and $Mg_4Zn_7$ in Mg–Zn alloys

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To understand the precipitates in Mg–Zn alloys, we perform first-principles calculations to investigate the stability and elastic properties of Laves $MgZn_2$ and monoclinic $Mg_4Zn_7$. We find that the relative stability of $MgZn_2$ and $Mg_4Zn_7$ is dependent on their compositions, implying that either one or both of the phases can exist within $\beta_1'$ precipitates. The elastic moduli indicate that the strain resistance of $MgZn_2$ and $Mg_4Zn_7$ is much greater than that of Mg.


*Keywords:* Magnesium alloy; Precipitation; First-principles calculation; Elastic behavior

Magnesium alloys, which offer a 30% weight reduction compared to aluminum alloys and a 75% weight reduction compared to steels, represent promising lightweight structural materials with potential automotive and aerospace applications. Mg–Zn alloys form the well-known ZK series of precipitation-hardening alloys. This series possesses the greatest precipitation hardening of Mg-based alloys due to the precipitation of a fine, rod-like binary $\beta_1'$ phase which can prevent the motion of dislocation and resist basal slip. In Mg–Zn alloys, with the addition of other elements such as rare earths, ternary phases form at the grain boundaries, and Mg–Zn binaries also form inside the grains. With overaging of Mg–Zn alloys, the $\beta_1'$ precipitate transforms into a plate-like $\beta_2'$ one.

Due to the importance of the $\beta_1'$ phase in hardening Mg–Zn alloys, many efforts have been made to characterize the crystal structure of this $\beta_1'$ phase. However, the crystal structures of such precipitates have been reported in the literature vary widely. A very early study showed that the rod-like $\beta_1'$ precipitates have a Laves $MgZn_2$ structure [1]. This argument is supported by recent experiments on Mg–Zn and Mg–Zn–X (X = Ca, Zr or Ag) alloys [2,3]. Mendis et al. observed that the rod-like $\beta_1'$ precipitates possess the structure of an $MgZn_2$ phase in Mg–Zn, Mg–Zn–Ca, Mg–Zn–Ag–Ca, Mg–Zn–Zr and Mg–Zn–Ag–Ca–Zr alloys aged to peak hardness at 160 °C [2,3]. However, other studies have demonstrated that the structures of $\beta_1'$ are based on a monoclinic $Mg_4Zn_7$ phase. Gao et al. showed that the $\beta_1'$ precipitates in a Mg–Zn alloy aged at 200 °C do not possess an $MgZn_2$ structure; instead, they possess a base-centred monoclinic structure based on the $Mg_4Zn_7$ phase [4]. At the same time, they found that $\beta_2'$ precipitates are distinct from $\beta_1'$ precipitates, and that the former do have an $MgZn_2$ structure. Similarly, Singh et al. found that the rod-like $\beta_1'$ precipitates in Mg–Zn–Y aged at 250 °C have a complex domain structure based on the structure of the monoclinic $Mg_4Zn_7$ phase [5]. In a subsequent work, they further demonstrated that, in the complex domain structures of the rod-like $\beta_1'$ precipitates in an Mg–Zn–Y alloy, the hexagonal Laves phase of $MgZn_2$ coexists with monoclinic $Mg_4Zn_7$ [6]. In addition, Mendis et al. found that the rod-like and blocky precipitates in Mg–Zn–Al alloys aged to peak hardness at 160 °C have an $Mg_4Zn_7$ structure [7].

It is clear that the structures of $\beta_1'$ precipitates that have been affected by different conditions are different and, furthermore, their evolution behaviour is complicated. The $MgZn_2$ and $Mg_4Zn_7$ phases are the main components of a $\beta_1'$ precipitate, while $MgZn_2$ is the main component of a $\beta_2'$ precipitate. Therefore, the crystal stability and elastic properties of these two phases are of

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fundamental importance for understanding precipitate structures and their hardening effects. The stability and electronic and elastic properties of $MgZn_2$ have received considerable attention with a motivation of understanding the precipitates in Mg–Zn alloys at the atomic scale [8,9]. However, the elastic properties of $Mg_4Zn_7$ and the stability of $Mg_4Zn_7$ relative to $MgZn_2$ are not well understood. In this paper, we report the results from first-principles calculations based on density functional theory for the enthalpies of formation and the elastic constants of $MgZn_2$ and $Mg_4Zn_7$. In particular, we discuss the stability dependence of the Laves phase and the monoclinic phase of Mg–Zn alloy on the stoichiometry of these two phases. From the calculated elastic constants and moduli, we also discuss the hardening effects of $MgZn_2$ and $Mg_4Zn_7$.

The first-principles calculations at a temperature of $T = 0$ K are based on density functional theory and performed using the Vienna Ab Initio Simulation Package [10,11] with a plane wave basis set. The electron exchange and correlation is described within the generalized gradient approximation [12,13], and the interaction between ions and electrons is described using the projector augmented wave method [14,15]. The Brillouin zone (BZ) integration is performed by the special $k$-point sampling of the Monkhorst–Pack type. For the BZs of Mg, Zn, $MgZn_2$, the $5 \times 1 \times 2$ supercell of $MgZn_2$ and $Mg_4Zn_7$, the $k$-point meshes of $12 \times 12 \times 8$, $12 \times 12 \times 8$, $8 \times 8 \times 6$, $2 \times 8 \times 3$ and $2 \times 8 \times 4$ are used. An energy cut-off of 380 eV is applied for all the calculations. Tests verify that the above setup is sufficient to provide superior accuracy in the present study.

The Laves phase of $MgZn_2$ has a hexagonal structure with the space group $P6_3/mmc$, whereas $Mg_4Zn_7$ is crystallized in the monoclinic structure with space group $C2/m$. Figure 1(a) and (b) shows the crystal structure of $MgZn_2$ along the $[11\bar{2}0]$ axis and the structure of $Mg_4Zn_7$ along the [0 1 0] axis, respectively. Through a detailed geometrical analysis, one can find that the Laves structure is built up by a series of face-sharing rhombic tiles (see point A). Such a rhombic tile can be decomposed into two smaller units that are known as Friauf polyhedrons [16]. (As shown in Fig. 1(c), the Friauf polyhedron is a tetracapped, truncated tetrahedron.) The monoclinic structure also contains the rhombic tile (see point B) and, in addition, another rhombic tile unit

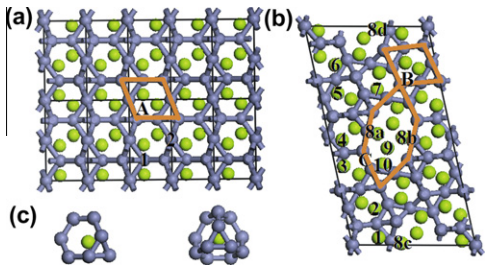


**Figure 1.** The structures of (a) the hexagonal Laves phase, (b) the monoclinic phase and (c) the Friauf polyhedron from different points of view. The black lines are cellular boundaries. The orange lines are included to facilitate the distinction between the rhombic and hexagonal units. The Zn atoms are in blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1.** The relative energies ($\Delta E$, in eV) of the substitution of Mg for Zn (i.e. $Mg_{Zn}$) in $MgZn_2$ and the substitution of Zn for Mg (i.e. $Zn_{Mg}$) in $Mg_4Zn_7$. All of the values are given with respect to the most stable configurations of $Mg_{Zn}$ and $Zn_{Mg}$. The substitutional sites in $MgZn_2$ and $Mg_4Zn_7$ are indicated in Fig. 1.

| | | | | | |
|---|---|---|---|---|---|
| Substitutional site | Zn1 | | | | Zn2 |
| $\Delta E(Mg_{Zn}$ in $MgZn_2)$ | 0 | | | | 0.07 |
| Substitutional site | Mg1 | Mg2 | Mg3 | Mg4 | Mg5 |
| $\Delta E(Zn_{Mg}$ in $Mg_4Zn_7)$ | 0.57 | 0.60 | 0.61 | 0.61 | 0.66 |
| Substitutional site | Mg6 | Mg7 | Mg8 | Mg9 | Mg10 |
| $\Delta E(Zn_{Mg}$ in $Mg_4Zn_7)$ | 0.64 | 0.66 | 0 | 0.35 | 0.57 |
| Substitutional sites | Zn (1 + 1)(s)[a] | | | Zn (1 + 1)(a)[a] | |
| $\Delta E(2\,Mg_{Zn}$ in $MgZn_2)$ | 0 | | | 0.10 | |
| Substitutional sites | Mg (8a + 8c) | Mg (8a + 8b) | | Mg (8a + 9) | |
| $\Delta E(2Zn_{Mg}$ in $Mg_4Zn_7)$ | 0 | 0.16 | | 0.29 | |

[a] (s) and (a) indicate that there are Mg atoms at separated sites and at

(see point C). The unit C, which is zinc-deficient relative to the Laves phase composition, servers to establish the composition of $Mg_4Zn_7$.

The thermal stability of $MgZn_2$ and $Mg_4Zn_7$ can be reflected by the formation enthalpies $\Delta H$, which are given by the energies of the phases relative to the composition-weighted average of the energies of the pure constituents each in their equilibrium crystal structures. $\Delta H$ is calculated as follows: $\Delta H = E_{tot} - x_{Mg}E^{Mg}_{eq} - x_{Zn}E^{Zn}_{eq}$, where $E_{tot}$, $E^{Mg}_{eq}$ and $E^{Zn}_{eq}$ are the total energies per atom of $Mg_{x_{Mg}}Zn_{x_{Zn}}$ binary, Mg, and Zn in their equilibrium crystal structures, respectively. $x_{Mg}$ and $x_{Zn}$ are the concentrations of the Mg and Zn atoms in the $Mg_{x_{Mg}}Zn_{x_{Zn}}$ binary phase, respectively. The formation enthalpy of the Mg solid solution with solute Zn atoms is 0.003 eV atom$^{-1}$. The formation enthalpies of stoichiometric $MgZn_2$ and $Mg_4Zn_7$ are $-0.145$ and $-0.141$ eV atom$^{-1}$, respectively; these enthalpies are much lower than the formation enthalpy of Mg solid solution with solute Zn atoms. This fact indicates that both $MgZn_2$ and $Mg_4Zn_7$ are more stable than the Mg solid solution with solute Zn atoms.

To examine the competition between $MgZn_2$ and $Mg_4Zn_7$ in both $\beta'_1$ and $\beta'_2$, we calculate the total energies of the two phases in various compositions. The concentrations of Zn in stoichiometric $MgZn_2$ and $Mg_4Zn_7$ are 63.63 and 66.67 at.%, respectively. To simulate the configurations of the binary phase with a Zn composition of 63–67 at.%, we consider that Zn is replaced by Mg in a Laves structure and that Mg is replaced by Zn in a monoclinic structure. First, we present the energetics of the substitution of Mg for Zn in $MgZn_2$ and the substitution of Zn for Mg in $Mg_4Zn_7$ in Table 1. Then we illustrate the most energetically favourable configurations of two phases in various compositions. Figure 1(a) shows the primitive cell of the Laves phase that is used to construct a $2 \times 5 \times 1$ supercell for calculating the total energies of the Laves phases with various compositions. The Laves structure of $MgZn_2$ has two symmetrically inequivalent Zn sites, i.e. Zn atoms occupy the Wyckoff positions of $6h$ ($x_1$, $2x_1$, 0.25) and $2a$ (0, 0, 0), which are labelled by 1 and 2, respectively, in Figure 1(a). Table 1 shows that the Mg substitution at site 1 in the Laves phase of $MgZn_2$ is energetically favourable compared to the Mg substitution at site 2. Any two substitutional Mg atoms that take place of the Zn atoms tend to occupy separated site 1. Naturally,