First-principles study on thermodynamic stability and electronic characteristics of long-period stacking ordered phases in Mg–Zn–Y alloys

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Abstract

A first-principles pseudopotential plane-wave method based on density functional theory has been used to investigate the thermodynamic stability and electronic characteristics of long-period stacking ordered (LPSO) phases in Mg–Zn–Y alloys. The obtained lattice constants of each LPSO phase considered are in good agreement with the experimentally determined values, with relative errors ranging from 0.21% to 2.0%. The calculated enthalpies of formation show that 14H and 18R phases can co-exist in the Mg–Zn–Y system, and the 18R phase is easier to form than the 14H phase while solidifying. But the 14H phase is more stable than the 18R phase by the calculation results of reaction energy. And the calculated results are in accord with the experiments for the thermodynamic stability of the two phases. The density of states of these phases reveals that the discrepancy in the stability of LPSO phases could be attributed to the variation of bonding electron numbers at low-energy region of Fermi level. In addition, the calculation of the charge density shows that the Zn–Y bond exhibits covalent feature in both 14H and 18R phases, and the covalent bonding of the 14H phase is stronger than that of the 18R phase, which means the 14H phase is more stable than the 18R phase.

Keywords: First-principles, LPSO phases, Mg–Zn–Y alloys, electronic characteristics

1. Introduction

Ternary alloys Mg–Zn–Y have attracted considerable attention recently due to their excellent mechanical properties and unique microstructures [1–4]. Kawamura et al. [1] reported $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ (at.%) alloy with high tensile strength which was produced by a rapid solidification processing. The alloy exhibited a remarkably high tensile strength of 610 MPa and elongation of 5% at room temperature, and the specific strength is four times as high as that of a commercial AZ91-T6 alloy. Yoshimoto et al. [2] also reported a magnesium alloy with a nominal composition of $\text{Mg}_{96}\text{Zn}_2\text{Y}_2$ that showed tensile strength of 390 MPa and elongation of 5% at room temperature, and of more than 300 MPa even at the elevated temperature of 473 K. Homma et al. [3] successfully developed $\text{Mg-1.8Gd-1.8Y-0.69Zn-0.16Zr}$ alloy by conventional hot extrusion, which presents an tensile strength of 542 MPa, proof stress of 473 MPa and elongation to failure of 8.0%. These excellent mechanical properties are considered to be due to the hexagonal close packed (hcp) Mg fine grain matrix of 100–200 nm in diameter, being homogeneously dispersed with Mg_{24}Y_5 fine particles less than 10 nm in diameter, and a novel long-period stacking order (LPSO) phases [4].

The LPSO phase in the Mg–Zn–Y system was reported to be 6H structure in early studies, which is monoclinic ($a = 5.6 \text{ \AA}$, $b = 3.2 \text{ \AA}$, $c = 15.6 \text{ \AA}$, and $\beta=88^\circ$), and has an ABCBCB' stacking sequence of the close-packed planes [5,6]. In subsequent studies [7,8], the 6H structure was found to be not correct, and 18R and 14H structures were proposed. The 18R structure was initially regarded to be identical to X-Mg₁₂ZnY phase found by Luo and Zhang [9]. Its unit cell was thought to be hexagonal ($a = 3.2 \text{ \AA}$, $c = 48.6 \text{ \AA}$), with an ACBCBCBACACACBABABA stacking sequence of the closely packed planes [7,8,9]. The 14H structure was reported to have a hexagonal lattice ($a = 3.21 \text{ \AA}$, $c = 36.94 \text{ \AA}$) [10], with its closely packed planes arranged in an ACBCBABABABCBACA stacking sequence. Recently, Gröbner et al. [11] found that the 18R is stable in the high temperature range from 753 to 483 °C, while the 14H is stable below 537 °C, and between 537 °C to 483 °C, the 18R and

14H can coexist in some special alloy compositions.

First-principles calculations based on density functional theory has been proven to be effective to investigate thermodynamic stability of the precipitates in magnesium alloys [12–15]. There have been some first-principles investigations in thermodynamic stability for LPSO phases [16–19]. Datta et al. [16] calculated cohesive energy of Mg with different stacking structures, and the results showed that the 6 l (6 layers) structure is most stable beside the 2 l structure. At the same time, they also found that the addition of 2 at.% Y leads to the 6 l structure more stable. Chen et al. [17] reported electronic characteristic and enthalpy of formation of 6H structure in Mg₉₇Zn₁Y₂ alloy, which revealed that Y element makes enthalpy of formation decrease whereas Zn element increases enthalpy of formation, so the thermodynamic stability of the 6H structure would be enhanced by the addition of Y element. Tang et al. [18] calculated 18R structure in Mg₉₇Zn₁Y₂ alloy, their results indicated that the 18R possesses higher thermodynamic stability because of the covalent bonding is formed among Mg-Mg, Mg-Y and Mg-Zn atoms. Iikubo et al. [19] investigated phase stability of different LPSO structures in Mg, and their results demonstrated that 14H and 18R structures become more stable than 2H. Although a lot of achievements of the first-principles study of LPSO phases have been obtained, many fundamental issues remain unsolved. For example, the stability relationships and electronic characteristics of LPSO phases with different structures.

In order to further understand the electronic characteristics and thermodynamic stability of the LPSO phases, investigate the phase equilibria of the Mg–Zn–Y system. In this paper, first-principles calculations based on density functional theory were used to investigate enthalpies of formation, density of states and charge density of 18R and 14H phases, due to the 18R and 14H are the most frequently observed LPSO phases in Mg–Zn–Y alloys. The thermodynamic stability of 18R and 14H are analyzed and discussed, moreover, the mechanism of stability was also explained through electronic characteristics. The results will provide useful data for analysis and design of Mg–Zn–Y alloys.

2. Models and methods of computation

The structural models of the 14H and 18R phases were determined by Egusa et al. [20], and they assumed space group and atom site symmetry. For the 14H phase, its space group is $P6_3/mcm$, the lattice constants are $a = b = 11.1 \text{ \AA}$, $c = 36.5 \text{ \AA}$, and its composition is $\text{Mg}_{35}\text{Zn}_3\text{Y}_4$. The 18R phase belongs to space groups $C2/m$, the lattice constants are $a = 11.1 \text{ \AA}$, $b = 19.3 \text{ \AA}$, $c = 16.0 \text{ \AA}$, and its composition is $\text{Mg}_{29}\text{Zn}_3\text{Y}_4$. The 14H and 18R phases contain 168 and 72 atoms in the primitive unit cell, respectively. The crystal structures of the 14H and 18R phases are shown in Fig. 1 [21], and atom coordinates are presented in Table 1.

Fig.1. Crystal structures of LPSO phases (a) 14H and (b) 18R. The red, blue and green balls represent Mg, Zn and Y atoms, respectively.

The present calculations are performed using Vienna Ab-initio Simulation Package (VASP) [22,23] with projector augmented plane wave (PAW) pseudopotential [24,25], and generalized gradient approximation (GGA) is used to treat with and describe the exchange-correlation interaction [26]. The atomic electron configuration for Mg treats 2p, 3s states as valence states, and the others are described by 4s, 3d valence states for Zn, 4s, 4p, 5s, 4d valence states for Y. The plane wave cutoff energy is set to 360 eV. Optimization of atomic positions and lattice constants are performed for 14H and 18R phases, all the structures are fully relaxed until the forces on all the atoms is less than $0.02 \text{ eV/\AA}$, and the total energy is less than 0.1 meV/atom . The k-point meshes of Brillouin zone sampling in a primitive cell are

based on the Monkhorst-Pack scheme. For 18R phase, the values of the k -point meshes are $6 \times 6 \times 4$ for geometry optimization and $10 \times 10 \times 6$ for the density of states. The k -point meshes of 14H phase are $4 \times 4 \times 1$ for geometry optimization and $6 \times 6 \times 2$ for the density of states.

Table 1

Atom fractional coordinates of 14H and 18R phases in Mg–Zn–Y alloys.

14H					18R				
atom	site	x	y	z	atom	site	x	y	z
Mg ₁	24 <i>l</i>	1/6	4/6	1/28	Mg ₁	8 <i>j</i>	2/36	1/12	1/12
Mg ₂	24 <i>l</i>	5/6	1/6	3/28	Mg ₂	8 <i>j</i>	2/36	3/12	1/12
Mg ₃	24 <i>l</i>	1/6	4/6	5/28	Mg ₃	8 <i>j</i>	2/36	5/12	1/12
Mg ₄	12 <i>k</i>	3/6	0	3/28	Mg ₄	8 <i>j</i>	11/36	2/12	1/12
Mg ₅	12 <i>k</i>	5/6	0	5/28	Mg ₅	8 <i>j</i>	11/36	4/12	1/12
Mg ₆	12 <i>k</i>	2/6	0	5/28	Mg ₆	8 <i>j</i>	3/36	2/12	3/12
Mg ₇	12 <i>j</i>	1/6	2/6	7/28	Mg ₇	8 <i>j</i>	3/36	4/12	3/12
Mg ₈	8 <i>h</i>	2/6	4/6	3/28	Mg ₈	8 <i>j</i>	12/36	1/12	3/12
Mg ₉	6 <i>g</i>	3/6	0	7/28	Mg ₉	8 <i>j</i>	12/36	3/12	3/12
Mg ₁₀	4 <i>c</i>	2/6	4/6	7/28	Mg ₁₀	8 <i>j</i>	30/36	1/12	3/12
Mg ₁₁	2 <i>a</i>	0	0	7/28	Mg ₁₁	8 <i>j</i>	7/36	2/12	5/12
Zn	12 <i>k</i>	5/6	0	1/28	Mg ₁₂	8 <i>j</i>	34/36	1/12	5/12
Y ₁	12 <i>k</i>	2/6	0	1/28	Mg ₁₃	8 <i>j</i>	34/36	3/12	5/12
Y ₂	4 <i>e</i>	0	0	3/28	Mg ₁₄	4 <i>i</i>	11/36	0	1/12
					Mg ₁₅	4 <i>i</i>	29/36	0	1/12
					Mg ₁₆	4 <i>i</i>	3/36	0	3/12
					Zn ₁	8 <i>j</i>	16/36	1/12	5/12
					Zn ₂	4 <i>i</i>	25/36	0	5/12
					Y ₁	8 <i>j</i>	7/36	4/12	5/12
					Y ₂	4 <i>i</i>	21/36	0	3/12
					Y ₃	4 <i>i</i>	7/36	0	5/12

3. Results and discussion

3.1. Lattice constants

The calculated lattice constants of the 14H and 18R phases are listed in Table 2, which are compared with experimental and other theoretical values. The calculated values of lattice constants for the 14H and 18R phases are in good agreement with the experimental results [20], and close to the calculated results in reference [27]. The relative errors with the experimental data range from 0.21% to 2.0%. It should be noted that all the experimental values are at room temperature. Although the addition of zero point energy and finite temperature usually lead to the change of equilibrium lattice constants, the agreement of calculation values with experimental results could reasonably reflect the accuracy of present calculations.

Table 2

The calculated lattice constants and the experimental values.

LPSO	Formula	Lattice constants (Å)		
		Present work	Calculated [27]	Experimental [20]
14H	$\text{Mg}_{35}\text{Zn}_3\text{Y}_4$	$a = 11.16$	$a = 11.15$	$a = 11.1$
		$b = 11.16$	$b = 11.15$	$b = 11.1$
		$c = 36.41$	$c = 36.36$	$c = 36.5$
18R	$\text{Mg}_{29}\text{Zn}_3\text{Y}_4$	$a = 11.17$	$a = 11.15$	$a = 11.1$
		$b = 19.34$	$b = 19.31$	$b = 19.3$
		$c = 16.31$	$c = 16.08$	$c = 16.0$

3.2. Enthalpies of formation and reaction energy

The alloying ability of crystal structure is correlated to its enthalpy of formation, if the enthalpy of formation is negative, then the formation of a compound from its elements usually is an exothermic process. Furthermore, the lower the enthalpy of formation is, the stronger the alloying ability. In order to evaluate the alloying abilities of the 14H and 18R phases, the enthalpies of formation were calculated [28], which can be calculated by the following expression:

$$\Delta H = (E_{\text{tot}} - N_{\text{Mg}} E_{\text{solid}}^{\text{Mg}} - N_{\text{Zn}} E_{\text{solid}}^{\text{Zn}} - N_{\text{Y}} E_{\text{solid}}^{\text{Y}}) / (N_{\text{Mg}} + N_{\text{Zn}} + N_{\text{Y}}) \quad (1)$$

where E_{tot} is the total energy of unit cell, and $E_{\text{solid}}^{\text{Mg}}$, $E_{\text{solid}}^{\text{Zn}}$, and $E_{\text{solid}}^{\text{Y}}$ are the energy per atom of the ground state structure of elemental Mg, Zn, and Y, respectively. N_{Mg} , N_{Zn} , and N_{Y} refer to the numbers of Mg, Zn, and Y atoms in each unit cell, respectively. The calculated enthalpies of formation from Eq. (1) are -0.0712 eV/atom and -0.0793 eV/atom for the 14H and 18R phases, and the negative values imply that the phases are energetically favorable from the point of view of thermodynamics, which means the 14H and 18R phases can exist and be stable. Meanwhile present results also indicate that the 18R phase has lower enthalpy of formation, suggesting a strong alloying ability.

In order to compare the thermodynamic stability of the 14H and 18R phases, the following reaction is necessary as their components are different:

Based on the above results, we also evaluated reaction energy when the 18R phase transforms into the 14H phase. The predicted reaction energy is -0.0034 eV/atom for the transformations of the 18R phase into the 14H phase. The negative values indicate that the reaction is exothermic, which indicates that the 14H phase is more stable than the 18R phase. These results are in agreement with the experimental ones [7,8,11].

3.3. Density of states

It is well known that the electronic density of states (DOS) of a system describes the number of states at each energy level which is available for statistical physics and condensed matter physics. For further understanding of the electronic characteristic and thermodynamic stability, the electronic density of states (DOS) of the 14H and 18R phases were calculated. The total and partial densities of states of the 14H and 18R are shown in Fig. 2, in which the Fermi energy is set to be zero energy and marked by vertical dash lines.

Fig.2. The total and partial electronic density of states of (a) 14H and (b)18R.

Fig. 2(a) demonstrates that the main bonding peaks of the 14H phase is located at energy range between -6.98 eV and 2.17 eV, and the bonding peak between -6.98 and -2.52 eV are mainly dominated by valence electron of Mg 3s, Mg 2p and Zn 4s orbits. While the bonding peaks between -2.52 and 2.17 eV originate from the hybridization of Mg 2p with Y 4d orbits, and are affected slightly by Zn 3p orbits. From Fig. 2(b), it can be seen that the main bonding peaks of the 18R is located at

energy range between -6.89 eV and 2.27 eV, the bonding peak between -6.89 and -2.31 eV are predominantly derived from Mg 3s, Mg 2p and Zn 4s orbits, the bonding peak between -2.31 and 2.27 eV originate from the hybridization of Mg 2p with Y 4d orbits, and are also affected slightly by Zn 3p orbits. From Fig.2, it can be seen that the density of states of the 14H and 18R phases are very similar in tendency. The Zn 4s, 3p orbits, Y 4d orbits, and Mg 3s, 2p orbits are broadly distributed in the entire region, while Zn 4d orbits, and Y 4s, 4p orbits are very weak in the whole region. Moreover, the present calculations also show that the main peaks of the 18R phase is similar to that of the 14H phase, which are also mainly dominated by the valence electrons of Mg 3s, 2p, Zn 4s, 3p and Y 4d orbits.

From Fig. 2(a), it can be seen clearly that there is a pseudo-gap near the Fermi energy level, which means coexistence of covalent and metallic bonds in the 14H phase [29]. The 14H phase is stable and has strong covalent and metallic mixing bonds due to the Fermi energy being at the pseudo-gap. However, from Fig. 2(b), it is found that the bonds in 18R is closer to metallic bonding than that in the 14H due to the Fermi energy being closer to one of the peaks of the total density of states.

Further analysis reveals that in the energy range between about -7.0 eV and 0 eV, the bonding electron number of per atom is 2.2175 for the 14H and 2.1501 for the 18R. Because the electron in low energy region of Fermi level are the mainly bonding electron, the more electrons in low energy region, the more intensified the interaction between valence electron of crystal, so the stability of crystal structure should be better [30–32]. The present results indicate that the 14H phase has the higher thermodynamic stability than the 18R, which coincides with the previously calculated results of reaction energy.

3.4. Charge densities

An important quantity which helps us characterize the bonds is the charge density. To gain more insight into the bonding behavior, the charge density distributions are also investigated. Fig.3 illustrates charge density distributions on the (0001) plane containing Y and Zn atoms of the 14H and 18R phases. The condensed charge concentrations around the Mg, Y and Zn atoms correspond to the semi-core states,

and contribute relatively little to the bonding. While the obvious overlaps of charge density between Zn-Y bonds further reveals covalent feature, suggesting a strong interaction between Zn and Y atoms, which is consistent with the observations of pseudo-gap around the Fermi energy level in DOS plots. In contrast to the Zn-Y bonds, there is no overlap of charge density distribution around Mg atoms, the almost uniform charge density distribution around Mg atoms is likely to be the metallic bond and can be well described by the nearly free electron model. These results are consistent with the DOS analysis described above. From Fig.3, it can be seen that the charge density between Zn and Y atoms in the 14H phase is more than that in the 18R phase. Therefore, the Zn-Y bonds in the 14H phase is stronger than that in the 18R phase, which lead to that the 14H phase is more stable than the 18R phase.

Fig.3. Charge density distributions on the (0001) plane of (a) 14H and (b) 18R phases.

4. Conclusion

In this paper, the thermodynamic stability and electronic characteristics of the LPSO phases in Mg–Zn–Y alloys were investigated by the first-principles methods. The calculated lattice constants of the 14H and 18R phases coincide with the corresponding experimental values. At the same time, the calculated enthalpies of

formation indicate that the 14H and 18R phases coexist in Mg–Zn–Y alloys, and the alloying ability of the 18R is stronger than that of the 14H. And the reaction energy shows that the 14H phase is more stable than the 18R phase. In addition, via calculations of the density of states (DOS) for the 14H and 18R phases, it is found that the bonding occurs mainly among the valence electrons of Mg 3s, 2p, Zn 4s, 3p and Y 4d orbits and the discrepancy in the thermodynamic stability of LPSO phases could be attributed to the bonding electron numbers at low energy of Fermi level. In addition, the charge density calculated for the 14H and 18R phases show that the Zn–Y bonds exhibit covalent feature, and the covalent bonds in the 14H phase is stronger than that in the 18R phase.

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