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Theoretical investigation of typical fcc precipitates in Mg-based alloys

Bi-Yu Tang [a,b,*], Na Wang [a,b], Wei-Yang Yu [a,b], Xiao-Qin Zeng [c], Wen-Jiang Ding [c]

[a] School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China
[b] Department of Physics, Xiangtan University, Hunan Province 411105, China
[c] Light Alloy Net Forming National Engineering Research Center, School of Materials Science and Engineering, Shanghai Jiaotong University, Shanghai 200030, China

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Abstract

First-principles calculations were performed to study structural, elastic and electronic properties of typical face-centered cubic (fcc) precipitates of Mg-based alloys (Mg_3Gd, $Mg_3Gd_{0.5}Y_{0.5}$ and $Mg_3Zn_3Y_2$) within the generalized gradient approximation. The calculated results show that the substitution of part of the Gd with Y in Mg_3Gd leads to a slight decrease in the cell volume (0.35%), and the lattice parameters obtained after full relaxation of crystalline cells are in good agreement with the experimental data. The calculated negative formation enthalpies and the cohesive energies show that these typical fcc precipitates of Mg-based alloys have good alloying ability and structural stability. According to the calculated density of states of these phases, it is found that the highest structural stability of $Mg_3Zn_3Y_2$ is attributed to an increase in the bonding electron numbers below the Fermi level. In addition, the elastic constants C_{ij} of these phases were also calculated, and the bulk modulus B, shear modulus G, Young's modulus E, Poisson's ratio v and anisotropy value A of polycrystalline materials were derived from the elastic constants. The mechanical properties are further discussed.

Keywords: Mg-based alloys; Fcc precipitates; First-principles calculation; Electronic structure; Mechanical properties

1. Introduction

Because magnesium alloys are lightweight structural materials with high specific strength and good stiffness, they have received increasing attention in the microelectronic, automotive and aerospace industries [1–3]. However, the application of magnesium alloys in modern industry is limited because of their poor mechanical properties at high temperature [4]. Over the past decade much effort has been devoted to improving the mechanical properties of Mg-based alloys. The addition of rare-earth (RE) elements in magnesium alloys has been known to improve their mechanical properties [5], and many precipitates have been found in RE-containing magnesium alloys that play a very important role in optimizing the microstructure and mechanical properties [4–7]. Mg–Gd systems are typical Mg–RE alloys, and are first investigated by Savitskii et al. [8]. The equilibrium solid solubility of Gd in magnesium is relatively high (4.53 at.% or 23.49 wt.% at 548 °C) and decreases exponentially with temperature (to 0.61 at.% or 3.82 wt.% at 200 °C), which could lead to the formation of the ideal system for precipitation hardening [9]. Recent studies have shown that Mg–Gd alloys have a creep resistance superior to that of alloys WE43 and QE22 in terms of steady-state creep rate [4]. Mg_3Gd is one of the most important alloy phases in the Mg–Gd system. Mg–Y alloys are more interesting as lightweight structural materials, and have been reported to have high strength at both room and elevated temperatures [10,11]. On the other hand, with the addition of other elements, the mechanical properties of Mg-based alloys can be improved further. For instance, the ternary Mg–Zn–Y alloy system has also been studied extensively and three kinds of ternary equilibrium phases

* Corresponding author. Address: School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China. Tel./fax: +86 732 8292195.
E-mail address: tangbiyu@xtu.edu.cn (B.-Y. Tang).

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have been found: the W-$Mg_3Zn_3Y_2$, Z-Mg_3Zn_6Y and X-$Mg_{12}ZnY$ phases [12]. In particular, the Mg–2.1Gd–0.6Y–0.2Zr (at.%) alloy reported by Anthony [13] shows considerable precipitation hardening, and its strength, elongation and creep resistance are far superior to those of the commercial alloy WE54 [14]. Recently, a new phase, $Mg_3Gd_{0.5}Y_{0.5}$, has been reported [15]. In spite of many experimental investigations on RE-containing magnesium alloys, there have been few theoretical studies.

First-principles calculations have become an important tool for the accurate study of the crystalline and electronic structures and mechanical properties of solids [16]. In the present work, we report a systematic investigation of the structural, electronic and elastic properties of typical face-centered cubic (fcc) precipitates of Mg-based alloys (Mg_3Gd, $Mg_3Gd_{0.5}Y_{0.5}$ and $Mg_3Zn_3Y_2$) by first-principles calculations, and the results are discussed in comparison with the available experimental data.

2. Method

The calculations were performed using the Vienna Ab Initio Simulation Package [17], based on density functional theory. We used the well established Perdew–Wang (PW91) version of the generalized gradient approximation (GGA) [18] to describe the exchange-correlation energy. The interaction between the valence electrons and the ions was described by using potentials generated with Blöchl's projector augmented wave (PAW) method [19]. The PAW potential used for Mg treats 3s, 2p states as valence states, and the other electron–ion interaction is described by 3d, 4s valence states for Zn, 4s, 4p, 5s, 4d valence states for Y, and 4f, 5p, 5d, 6s valence states for Gd. A plane-wave energy cutoff was set at 300 eV for Mg_3Gd and $Mg_3Gd_{0.5}Y_{0.5}$, and at 400 eV for $Mg_3Zn_3Y_2$. The Brillouin zone integrations used Monkhorst–Pack grids [20] with $8 \times 8 \times 8$ for optimizing geometry and calculating elastic constants, and $12 \times 12 \times 12$ for the density of states (DOS) calculation.

For the structural relaxation, the first-order Methfessel–Paxton [21] method with a width of 0.2 eV was used, and the density of states (DOS) and total energy calculations were performed using the linear tetrahedron method with Blöchel correction [22]. Atomic geometry relaxation was performed using the conjugate gradient method, until the total forces on each ion were less than 0.02 eV $Å^{-1}$.

3. Result and discussion

3.1. Equilibrium properties

Mg_3Gd phase belongs to an isostructure of BiF_3 with the Fm-3m space group [23], and $Mg_3Gd_{0.5}Y_{0.5}$ results from substitution of part of the Gd by Y in Mg_3Gd, keeping its fcc structure [15]. $Mg_3Zn_3Y_2$ alloy is a partially ordered $AlMnCu_2$-type fcc structure also with the Fm-3m space group [12]. Starting from the above fcc structure, crystal structures were first optimized with full relaxation of cell shape and atomic positions. The equilibrium volume V_0 and bulk modulus B_0 of $Mg_3Zn_3Y_2$, Mg_3Gd and $Mg_3Gd_{0.5}Y_{0.5}$ were determined by fitting the total energy calculated at different lattice constant values to a Birch–Murnaghan equation of state [24]. The computed equilibrium parameters are listed in Table 1. Our results agree very well with the experimental data. The results of our calculations also reveal a volume per atom in $Mg_3Gd_{0.5}Y_{0.5}$ of 0.35% (lattice constant of about 0.14%) smaller than that of bulk Mg_3Gd, indicating that a small addition of Y to Mg_3Gd leads to contraction of the lattice.

The structural stability of crystal is correlated to its cohesive energy E_{coh}, which is defined as the work that is needed when the crystal decomposes into the single atom. Hence, the bigger the cohesive energy, the more stable the crystal structure [25]. In this work, the cohesive energies (E_{coh}) of Mg_3Gd, $Mg_3Gd_{0.5}Y_{0.5}$ and $Mg_3Zn_3Y_2$ crystal cells were calculated by

$$E_{coh}^{ABC} = (E_{tot} - N_A E_{atom}^A - N_B E_{atom}^B - N_C E_{atom}^C) / (N_A + N_B + N_C) \quad (1)$$

where E_{tot} is the total energy of the compound, and E_{atom}^A, E_{atom}^B, E_{atom}^C are the total energies of atoms A, B and C in the freedom states. N_A, N_B and N_C refer to the numbers of A, B and C atoms in each unit cell. The results of the cohesive energy calculation are listed in Table 2. From the calculated values, we find that $Mg_3Zn_3Y_2$ has a cohesive energy that is 0.012 and 0.026 eV $atom^{-1}$ lower than that of Mg_3Gd and $Mg_3Gd_{0.5}Y_{0.5}$, respectively. Hence, of the three phases, $Mg_3Zn_3Y_2$ phase has the highest structural stability, followed by Mg_3Gd and finally $Mg_3Gd_{0.5}Y_{0.5}$.

In order to evaluate the alloying abilities of the present compounds, we calculate the formation enthalpies ΔH [25], which can be calculated for ternary alloy as

$$\Delta H_{ABC} = (E_{tot} - N_A E_{solid}^A - N_B E_{solid}^B - N_C E_{solid}^C) / (N_A + N_B + N_C) \quad (2)$$

Table 1
Calculated and experimental lattice constants a (Å), volumes (Å^3) and bulk modulus B_0 (GPa) for Mg_3Gd, $Mg_3Gd_{0.5}Y_{0.5}$ and $Mg_3Zn_3Y_2$ in the fcc structure

	Mg_3Gd		$Mg_3Gd_{0.5}Y_{0.5}$		$Mg_3Zn_3Y_2$	
	Present.	Expt.	Present.	Expt.	Present.	Expt.
a	7.330	7.324	7.320	–	6.924	6.848
V	393.48	392.87	392.11	–	334.86	321.14
B_0	40.7	–	40.4	–	54.2	–

Table 2
Total free energy E_0, cohesive energy E_{coh} and formation enthalpy ΔH of Mg_3Gd, $Mg_3Gd_{0.5}Y_{0.5}$ and $Mg_3Zn_3Y_2$

Compound	E_{tot} (eV)	E_{coh} (eV $atom^{-1}$)	ΔH (eV $atom^{-1}$)
Mg_3Gd	−38.138	−2.329	−0.1002
$Mg_3Gd_{0.5}Y_{0.5}$	−41.692	−2.315	−0.0974
Mg_3 Zn_3Y_2	−45.674	−2.341	−0.2742