First-Principle Calculations of the MgYA_4 ($A = \text{Co}$ and Ni) Phase with AuBe_5 -Type Structure

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Abstract First-principles calculations have been performed to study the structural, mechanical and magnetic properties of the MgYCo_4 and MgYNi_4 phases in AuBe_5 -type structure. The obtained values of cohesive energy as well as formation energy prove that the MgYCo_4 and MgYNi_4 phases have a good combination of structural stability and alloying ability, which is also supported by electronic structure. It is found that the magnetic moment of the MgYCo_4 phase is $19.06 \mu_B$ per unit cell mainly owed to the $3d$ state of Co atom, and the MgYNi_4 phase exhibits no magnetism. Both the trigonal shear constant C_{44} and the shear modulus G of the MgYNi_4 phase are larger than those of the MgYCo_4 phase. Plasticity of alloys has been estimated by the C_{11} – C_{12} and Young's modulus E , and C_{12} – C_{44} , shear to bulk modulus ratio G/B and Poisson's ratio ν have been studied to predict the ductility of alloys. According to the calculated results, the MgYCo_4 phase has better plasticity as well as ductility, compared with the MgYNi_4 phase.

KEY WORDS: Ductility; Plasticity; Elastic modulus; Magnesium alloy; Electrical and magnetic properties

1 Introduction

Because of high strength and high ductility, intermetallic magnesium compounds with long-period stacking order (LPSO) structures have attracted significant attention and been studied for long time [1–3]. Recently, many LPSO structures in Mg – TM – Y ternary alloys ($\text{TM} = \text{Zn}, \text{Cu}, \text{Ni}$

or Co) have been found and intensively investigated [4–6]. At room temperature, the yield strength of $\text{Mg}_{97}\text{Zn}_1\text{Y}_2$ (at%) alloy with LPSO structure reaches a level of 600 MPa (5% elongation) and $\text{Mg}_{90.5}\text{Ni}_{3.25}\text{Y}_{6.25}$ (at%) alloy with an 18R LPSO structure exhibits a yield strength of 460 MPa (8% elongation) [7, 8]. Several experiments have been carried out to investigate the microstructure and mechanical properties especially in Mg – Co/Ni – Y ternary alloys, and some important precipitates have been reported [9–11]. The MgYNi_4 phase ($a = 0.701 \text{ nm}$) reported by Aono et al. is an AuBe_5 -type Laves phase structure, and its hydrogen content reaches a level of 1.05 wt% with -35.8 kJ/mol H_2 enthalpy of hydride formation [12]. The MgYCo_4 phase ($a = 0.707 \text{ nm}$) found in $\text{Mg}_{88}\text{Co}_5\text{Y}_7$ (at%) alloy has the same crystallographic structure as the MgYNi_4 phase, with a 0.86% increase in lattice parameter [13]. Although the atomic number of Co atom is next to Ni atom, the mechanical and magnetic properties of the MgYCo_4 phase may be different from that of the MgYNi_4 phase. Nevertheless, there is little information reported in the literature.

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It is well known that the first-principles calculations based on DFT is a reliable tool to estimate the mechanical properties of alloys. Single-crystal elastic constants can be firstly obtained by applying infinitesimal strains and then can give the values of polycrystalline elastic modulus according to proper symmetry relationship [14]. Shear modulus to bulk modulus ratio (G/B) introduced by Pugh [15] is used to estimate the brittleness and ductility of alloys. The G/B of brittle material is generally higher than 0.57, while values <0.57 indicate ductility [16]. In this work, we carry out ab initio calculations on the structural, magnetic, mechanical and electronic properties of the MgYCo_4 and MgYNi_4 phases with typical face-centered cubic (fcc) crystal structure, and the calculated results are compared with experiments. The study will give a powerful guidance as to the investigation of Mg–TM–RE alloys, and also for the future estimation of the MgYCo_4 and MgYNi_4 phases.

2 Method

The first-principles calculations were performed based on density functional theory provided in the Vienna ab initio simulation package (VASP) [17]. Generalized gradient approximation (GGA) in Perdew–Burke–Ernzerhof (PBE) version is selected to describe the exchange–correlation energy functional, giving reliable values of magnetic moments for transition metals [18]. Projector augmented wave (PAW) method has been used to describe the ion–electron interactions [19], treating $3s$, $3d4s$ and $4s4p5s4d$ states as valence states for Mg, Co/Ni and Y, respectively. The kinetic energy cutoff has been tested and is set to 350 eV, with Monkhorst–Pack grid sampling the Brillouin zone (BZ) [20]. The $10 \times 10 \times 10k$ -point mesh and $12 \times 12 \times 12k$ -point mesh have been selected for structural optimization and density of states (DOS) calculation, respectively. Firstly, the first-order Methfessel–Paxton [21] method has been used to optimize the structures, with the atomic positions fully relaxed until the total forces are less than 0.01 eV/Å. Then, the DOS calculations have been performed by tetrahedron method with Blöchl [22] correction. In this work, the spin polarization effect has been considered for all calculations. The calculated lattice constants of pure metals (Co: $a = 2.487$ Å, $c = 4.070$ Å; Ni: $a = 3.517$ Å) are in good agreement with the experiments (Co: $a = 2.507$ Å, $c = 4.038$ Å; Ni: $a = 3.524$ Å) [23, 24], where the difference is found to be around 0.5%. Furthermore, the calculated magnetic moments per atom of pure Ni and Co are 0.60 μ_B and 1.49 μ_B , respectively, and provide a good accordance with the literatures [24, 25]. All these show that the above method of calculation is reliable.

3 Results and Discussion

3.1 Structural Properties

The space group of the MgYA_4 (where $A = \text{Co}$ and Ni) phases with AuBe_5 -type structure is $F\bar{4}3m$ (Space No. 216) with unit cell containing 4 Mg atoms, 4 Y atoms and 16 A atoms, as shown in Fig. 1. The calculated and experimental crystallographic data are listed in Table 1, and the difference is found to be only -0.15% [12, 13]. The equilibrium structural constants presented in Table 2 show that MgYNi_4 phase compared with MgYCo_4 phase has smaller lattice constant as well as equilibrium volume. Furthermore, the bulk modulus B_0 of both phases was obtained (see Table 2) through the Birch–Murnaghan equation of state (BM–EOS) [26] by fitting the total energy calculated at different lattice volume, as shown in Fig. 2.

Fig. 1 Crystal structure of AuBe_5 -type for MgYNi_4 (MgYCo_4) phase, where the yellow, red and blue balls represent Mg, Y and Ni (Co) atoms, respectively

Table 1 Calculated crystallographic parameters of MgYCo_4 and MgYNi_4 phases, and compared with experimental data, the coordinates are $(0, 0, 0) + (0.0, 0.5, 0.5) + (0.5, 0.0, 0.5) + (0.5, 0.5, 0.0)$

Phase	Multiplicity, Wyckoff letter		x	y	z
MgYCo_4	Y, 4a	Relaxed	0	0	0
		Expt.	0	0	0
	Mg, 4c	Relaxed	0.2500	0.2500	0.2500
		Expt.	0.2500	0.2500	0.2500
	Ni, 16e	Relaxed	0.6243	0.6243	0.6243
		Expt.	0.6250	0.6250	0.6250
MgYNi_4	Y, 4a	Relaxed	0	0	0
		Expt.	0	0	0
	Mg, 4c	Relaxed	0.2500	0.2500	0.2500
		Expt.	0.2500	0.2500	0.2500
	Co, 16e	Relaxed	0.6237	0.6237	0.6237
		Expt.	0.6250	0.6250	0.6250

Table 2 Structural parameters for MgYNi₄ and MgYCo₄ phases

Phase		a (Å)	V_0 (Å ³)	B_0 (GPa)	E_c (eV/atom)	ΔH (eV/atom)	M (μ _B /cell)
MgYCo ₄	Present.	7.02	346	127	−4.82	−0.13	19.65
	Expt [13].	7.07	353	—	—	—	—
MgYNi ₄	Present.	7.01	344	129	−4.62	−0.39	0
	Expt [12].	7.01	344	—	—	—	—

Fig. 2 Curve fitted by BM-EOS equation for the MgYCo₄ **a** MgYNi₄ **b** phases, where the *black dots* represent the calculated values

The cohesive energy (E_c) estimating stability of precipitates as well as the formation energy (ΔH) predicating the alloying ability have been discussed and defined in Refs. [16, 27] as $E_c = (E - 4E_a^{\text{Mg}} - 4E_a^{\text{Y}} - 16E_a^{\text{A}})/24$ and $\Delta H = (E - 4E_{\text{Mg}} - 4E_{\text{Y}} - 16E_{\text{A}})/24$, where E , E_a^{Mg} , E_a^{Y} , E_a^{A} are the total energies of the phase, isolated atom Mg, Y and A, respectively. E_{Mg} , E_{Y} and E_{A} are the energy per atom of solid Mg, Y and A, respectively. The negative cohesive energy and formation energy (see Table 2) for both phases indicate that the MgYNi₄ and MgYCo₄ phases have a good combination of structural stability and alloying ability, giving a good accordance with the experiments [12, 13].

3.2 Mechanical Properties

Using density functional theory, the elastic parameters have been discussed and obtained by fitting the curve of the energy versus strain. The strain energy ($E(\varepsilon)$) can be Taylor expanded as $E(\varepsilon) = E(0) + \frac{V_0}{2} \sum_{ij=1}^6 C_{ij} e_i e_j$, where V_0 and $E(0)$ are the equilibrium volume and equilibrium energy of unit cell, respectively. C_{ij} s are the elastic constants, and strain ε is a 3×3 matrix containing six independent components e_i as followed [28].

Table 3 Three kinds of strain used for unit cell in present work

Strain	Parameters (unlisted $e_i = 0$)	$\Delta E/V_0 - 0$ (δ^2)
$\varepsilon^{(1)}$	$e_1 = e_2 = \delta$, $e_3 = [(1 + \delta)^{-2} - 1]$	$3(C_{11} - C_{12})\delta^2$
$\varepsilon^{(2)}$	$e_1 = e_2 = e_3 = \delta$	$3(C_{11} + 2C_{12})\delta^2/2$
$\varepsilon^{(3)}$	$e_6 = \delta/2$, $e_3 = \delta^2(1 - \delta)^{-1}$	$(C_{44}\delta^2)/2$

$$\varepsilon = \begin{pmatrix} e_1 & e_6 & e_5 \\ e_6 & e_2 & e_4 \\ e_5 & e_4 & e_3 \end{pmatrix}. \quad (1)$$

The MgYNi₄ and MgYCo₄ phases with cubic structure contain three independent elastic constants, C_{11} , C_{12} and C_{44} , and three kinds of strains have been applied (see Table 3) [29], where the infinitesimal distortion for $C_{11} - C_{12}$ and $C_{11} + 2C_{12}$ is 0, ± 0.02 and ± 0.04 with strains 3 being 0, ± 0.04 and ± 0.08 .

It can be seen from Table 4 that all of the calculated C_{ij} s for both phases are positive and $(C_{11} - C_{12}) > 0$ meeting the stability criteria of cubic crystal [28], as well as giving a consistent results with the cohesive energy. Furthermore, the bulk modulus (B) of both phases obtained by $B = (C_{11} + 2C_{12})/3$ is 122 GPa, exhibiting a good agreement with that fitted from BM-EOS.

Table 4 Single-crystal and polycrystalline elastic constants

Phase	C_{11}	C_{12}	C_{44}	B	G	G/B	E	ν
MgYCo ₄	158	104	48	122	38	0.31	103	0.36
MgYNi ₄	184	91	65	122	56	0.46	146	0.30

For cubic structure, polycrystalline parameters can be deduced from C_{11} , C_{12} and C_{44} by the accurate Hershey's averaging method [30], where the shear modulus G , Young's modulus E and Poisson's ratio ν are calculated as followed:

$$8G^3 + (5C_{11} + 4C_{12}G^2) - C_{44}(7C_{11} - 4C_{12})G - C_{44}(C_{11} - C_{12})(C_{11} + 2C_{12}) = 0. \quad (2)$$

$$E = 9GB/(3B + G). \quad (3)$$

$$\nu = (E - 2G)/2G. \quad (4)$$

Figure 3 displays the obtained trigonal shear constant C_{44} , shear modulus G , Young's modulus E and bulk modulus B . It is found that both C_{44} and G of the MgYNi₄ phase are larger than that of the MgYCo₄ phase, exhibiting a consistent trend with the literature [14]. It is also important to note that the MgYNi₄ phase exhibits a decrease in Poisson's ratio ν (see Table 4) and an increase in both shear modulus G and Young's modulus E . Both $C_{11}-C_{12}$ and E can predicate the plasticity of alloys, where the lower the value is, the better the plasticity will be. The $C_{11}-C_{12}$, $C_{12}-C_{44}$ and E of both phases are plotted in Fig. 4. Compared with the MgYNi₄ phase, the MgYCo₄ phase exhibits a decrease of 29.5% for E and 41.9% for

Fig. 3 Trend of calculated C_{44} , G , E and B for MgYCo₄ and MgYNi₄ phases **Fig. 4** Comparison of calculated $C_{11}-C_{12}$, E and $C_{12}-C_{44}$ for MgYCo₄ and MgYNi₄ phases

$C_{11}-C_{12}$, implying that MgYCo₄ phase has a better plasticity. $C_{12}-C_{44}$, G/B ratio and Poisson's ratio ν are three important parameters indicating the brittleness and ductility of alloys. It is found that for both phases, the value of $C_{12}-C_{44}$ is positive (see Fig. 4), the G/B ratio is smaller than 0.57 and the Poisson's ratio ν is near 0.5 (see Table 4), giving a consistent estimation of the ductility of both phases. Furthermore, the MgYCo₄ phase with a smaller G/B ratio and a bigger Poisson's ratio ν has a better ductility.

3.3 Magnetic Properties and Electronic Structures

The magnetic moments of the MgYCo₄ and MgYNi₄ phases have been calculated and listed in Table 2. The MgYCo₄ phase has the magnetic moments per atom at $0.79 \mu_B$, while MgYNi₄ alloy displays none magnetism. Figure 5 depicts the partial magnetic moments of the MgYCo₄ phase, including $-0.096 \mu_B$ for Mg atoms, $-1.284 \mu_B$ for Y atoms and $21.507 \mu_B$ for Co atoms. It can be seen that the direction of the spin polarization of Mg and Y atoms is opposite to that of the Co atoms, and the total magnetic moments of MgYCo₄ is mainly dependent on the Co atoms.

The total density of states (DOS) and partial density of states (PDOS) for MgYCo₄ and MgYNi₄ alloys, as shown in Fig. 6, are useful parameters to characterize the magnetic properties and structural properties. The total DOS, the d state of Y and Co/Ni atoms are marked by black, green and red solid lines, respectively. The value of electronic states for Mg atoms is too small, and it is not been plotted. From Fig. 6, it can be found that the Fermi level for both phases are occupied and dominantly contributed by $3d$ state in transition elements (Ni/Co), exhibiting a

Fig. 5 Partial magnetic moments (μ_B /unit cell) of the MgYCo₄ phase

metallic bonding character. The asymmetric trend of the spin-down state for the MgYCo₄ phase in Fig. 6, compared with the spin-up state, leads to a different amount of valence electrons at Fermi level, and thus results in the magnetic moment for the MgYCo₄ phase. It is found that the valence electron concentration for MgYCo₄ is 7.02 electrons per atom, while that of MgYNi₄ is 7.63 electrons per atom. More valence electrons result in stronger metallic bonding [31], and thus lead to a stable structure. Hence, the MgYNi₄ phase with more valence electrons has a better structural stability than the MgYCo₄ phase, exhibiting a good agreement with the results in Sect. 3.1. These DOS data of MgYCo₄ and MgYNi₄ alloys will give useful guidance for future measurements.

The charge densities of both phases were calculated and are shown in Fig. 7, where the isosurface value has been set to $\pm 0.035 \text{ eV/\AA}^3$. Losing electrons are characterized by green color, where brown color is representative of gaining electrons. We find the more complicated trend of charge transferring for co (Ni) atoms, compared with Mg atoms and Y atoms in both phases, indicating the strong interaction among the co (Ni) atoms, and thus are in agreement with the results from the DOS structures shown in Fig. 6. Furthermore, Ni–Ni bonds in the MgYNi₄ phase, stronger than Co–Co bonds in the MgYCo₄ phase, may lead to a decrease in lattice parameters and an increase in shear modulus for the MgYNi₄ phase.

4 Conclusions

Using Vienna ab initio simulation package (VASP), the structural, elastic and magnetic properties of the MgYCo₄ and MgYNi₄ phases have been calculated and analyzed. The obtained equilibrium structural parameters of both phases exhibit a good agreement with experiments. The MgYNi₄ phase with a lower cohesive energy shows a better structural stability than the MgYCo₄ phase. From the DOS structure, it is found that the better structural stability of the MgYNi₄ phase is owed to a bigger valence electron concentration. The spin-down states of Co atoms at Fermi level are larger than that of spin-up states with the major peak located below the Fermi level, leading to the magnetic moments for the MgYCo₄ phase. The calculated elastic data show that both C_{44} and G of the MgYNi₄ phase are larger than that of the MgYCo₄ phase, and the MgYCo₄ phase with smaller valence electron concentration exhibits

Fig. 6 Total and partial density of states for the MgYCo₄ **a** MgYNi₄ **b** phases, respectively

Fig. 7 Charge densities for MgYCo₄ **a** MgYNi₄ **b** phases with isosurface at $\pm 0.035 \text{ eV/\AA}^3$

an increase in Poisson's ratio and a decrease in both of shear and Young's modulus. The obtained Poisson's ratio ν , Young's modulus E and C_{11} – C_{12} show that the MgYCo₄ phase exhibits a better plasticity. The values of G/B ratio and C_{12} – C_{44} indicate that both phases are ductile alloys, while the MgYCo₄ phase has a better ductility than MgYNi₄ Phase.

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