

The Structures and Properties of Y-Substituted Mg₂Ni Alloys and Their Hydrides: A First-Principles Study

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Received 11 December 2015; accepted 22 January 2016; published 25 January 2016

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Abstract

The structures and properties of Y-substituted Mg₂Ni alloys and the corresponding hydrides are investigated by a first-principles plane-wave pseudopotential method within density functional theory. Results show that Mg₂Ni has the best structural stability when Y atom occupies the Mg(6f) lattice sites. The calculated enthalpies of formation for Mg₂Ni, Mg₂NiH₄ and Mg₁₅YNi₈H₃₂ are -51.612, -64.667 and -62.554 kJ/mol, respectively. It is implied that the substitution of Y alloying destabilizes the stability of the hydrides. Moreover, the dissociated energies of H atoms are decreased significantly, indicating that Y alloying benefits the improvement of the dehydrogenating properties of Mg₂Ni hydrides. The calculation and analysis of the electronic structures suggest that there is a stronger interaction between H and Ni atoms than the interaction between H and Mg atoms in Mg₂NiH₄. However, the Ni-H bond is weakened by the substitution of Y. Therefore, the substitution is an effective technique to decrease the structural stability of the hydrides and benefit for hydrogen storage.

Keywords

Mg₂Ni Alloys, Y Substitution, Hydrides, First-Principles

1. Introduction

Due to rich reserves in the earth's crust, high hydrogen capacity (3.6 wt%), light weight and low cost, Mg₂Ni-type alloy hydrides remain as attractive hydrogen storage materials [1] [2]. However, the practical application of

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the alloy materials has not been achieved because of unfavorable thermodynamics, poor hydrogenation/dehydrogenation kinetics and releasing undesirable by-products [3].

Many researches have been devoted to overcoming these drawbacks and improving the properties of hydrogen storage via modifying microstructure by mechanical alloying [4], alloying with other elements [5] [6], adding catalysts [7] and composite structures [8]. The effects of transition metals including Cu, Co, Mn, Y, Ti, Nb and Crelements [9]-[12] on the hydrogen storage properties of Mg-based metal hydrides are investigated and discovered that the properties of hydrogen storage are improved by alloying with a small amount of transition metals in different degrees.

It is believed that alloying of Mg_2Ni with transition metals is beneficial to improve the hydrogenating and dehydrogenating kinetics. The electronic structure of element Y is $4d^15s^2$ and it can be incorporated into the metal boride. In addition, its chemical properties and physical performance are similar to La which can be used as an alloy element for hydrogen storage. The density and cohesive energy of Y atom are also relatively small. Therefore, Y has great potential to improve the performance of Mg_2Ni alloy and its hydride. Kalinichenka *et al.* [13] studied that Y can be solved in Mg_2Ni and the Mg-Ni-Y alloy exhibits higher dehydrogenation rates comparing with that of the Mg-Ni alloy. Song *et al.* [14] reported the microstructure and the hydrogenation properties of melt-spun $Mg_{67}Ni_{33-x}Y_x$ alloys and found that the hydrogen storage capacity and kinetics of Mg_2Ni are improved with Y doping. Zhang *et al.* [15] investigated that the substitution of Y for Mg had an insignificant effect on the activation ability of the Mg_2Ni -type alloys, but it dramatically improved the cycle stability of the as-milled alloys. These experiments proved that Y plays an important role in improving the properties of Mg_2Ni alloy for hydrogen storage. Thus, my understanding is that, alloying of Mg_2Ni with Y can be expected to improve some performances of hydrogen absorption/desorption capacity and kinetics significantly.

In recent years, a number of theoretical investigations about the doped/substituted complex hydrides using first-principles calculations have been reported [16]-[19]. A first-principles study on the structures and properties of hydrogen storage alloy Mg_2Ni , of aluminum and silver substituted alloys $Mg_{2-x}M_xNi$ ($M = Al$ and Ag), and of their hydrides Mg_2NiH_4 , $Mg_{2-x}M_xNiH_4$ was performed by Zeng *et al.* [20]. Their results show that the hydrogen storage capacity is decreased by the substitution and the substitution destabilizes the hydrides. However, there are no available theoretical reports about the structures and properties of Y substituted Mg_2Ni alloys and their respective hydrides to the authors' knowledge. The models are new for the materials to store hydrogen.

We focus primarily on the stable configuration of Mg_2Ni alloys with Y substitution and determine the optimum position of Y. Furthermore, the energies, enthalpies of formation and electronic structures of Y alloying Mg_2Ni and its hydrides are also calculated and analyzed using a first-principles plane-wave pseudo potential simulations based on the density functional theory in this paper. These simulations are beneficial to improve our understanding of the effects of substitution on the properties of Mg_2Ni , and of the design about advanced magnesium-based hydrogen storage materials.

2. Computational Details

2.1. Computational Model

The crystal structure of Mg_2Ni is hexagonal and its space group is $P6_222$ (No.180) [21], as shown in **Figure 1(a)**. The lattice constants of Mg_2Ni are $a = b = 5.205 \text{ \AA}$, $c = 13.236 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. There are 12 Mg and 6 Ni atoms existing in the unit cell of Mg_2Ni . The spatial positions Mg and Ni atoms are respectively $6f(0.5, 0, 0.1187)$, $6i(0.16, 0.324, 0)$ and $3b(0, 0, 0.5)$, $3d(0.5, 0, 0.5)$. Single Y atom substituting for Mg and Ni atoms are investigated respectively. Moreover, it has been shown that Mg_2NiH_4 forms readily by hydrogenating the alloy Mg_2Ni [22]. The space group of Mg_2NiH_4 is monoclinic $C2/c$ (No.15) and the lattice constants are $a = 14.343 \text{ \AA}$, $b = 6.404 \text{ \AA}$, $c = 6.483 \text{ \AA}$, $\beta = 113.52^\circ$, as shown in **Figure 1(b)**. 16 Mg, 8 Ni and 32 H atoms are in the unit cell of Mg_2NiH_4 where Mg occupying the $8f$, $4e$, $4e$ sites and Ni the $8f$ site and H the $8f$, $8f$, $8f$, $8f$ sites [23] [24]. The new systems of Y alloying Mg_2NiH_4 are studied.

2.2. Computational Method

All the density-functional theory (DFT) calculations are performed using a plane-wave basis set with the projector augmented plane wave (PAW) method as implemented in the Vienna *ab initio* simulation package (VASP)

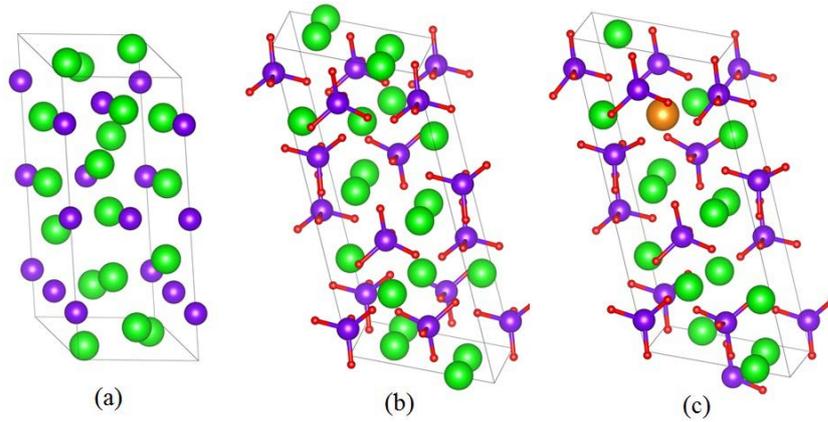


Figure 1. Structures of (a) Mg_2Ni , (b) Mg_2NiH_4 , (c) $\text{Mg}_{15}\text{YNi}_8\text{H}_{32}$ (where green, purple, red and orange balls denote Mg, Ni, H and Y atoms, respectively).

[25]-[27]. Projector Augmented Wave (PAW) potentials are used to treat the core-valence interaction [28]. The PW91 [29] [30] generalized gradient approximation (GGA) is employed for the exchange-correlation functional. The electronic wave functions are expanded by plane waves with a kinetic energy cutoff of 350 eV to attain the required convergence. All of the self-consistent loops are iterated until the total energy difference of the systems between the adjacent iterating steps is less than 10^{-7} eV. The Brillouin zone is sampled by $6 \times 6 \times 2$ mesh points in k-space based on Monkhorst-Pack scheme [31] for all systems. The valence electrons of $1s$ for H, $2p$ and $3s$ for Mg, $3p$, $3d$ and $4s$ for Ni, and $4d$ and $5s$ for Y are considered in the calculations.

3. Results and Discussions

3.1. The Structure of Substituted Mg_2Ni by Y

In order to check the accuracy of the calculations, we first optimize the structure of Mg_2Ni alloy and its hydride and compare the calculated lattice parameters with those determined experimentally. Then we consider the substitution of Mg and Ni by Y in independent spatial positions respectively. To single out a scenario that is most likely responsible for the stabilization of the crystal structure, the lattice parameters and enthalpies of formation ΔH for each case are calculated. The ΔH is calculated by taking the difference in total electronic energy of the products and the reactants [32]:

$$\Delta H = \sum_{\text{products}} E_p - \sum_{\text{reactants}} E_r \quad (1)$$

In the case of the crystal structure $\text{Mg}_x\text{Y}_y\text{Ni}_z$ which including $x\text{Mg}$, $y\text{Y}$, $z\text{Ni}$, the enthalpies of formation are calculated by the following equation:

$$\Delta H(\text{Mg}_x\text{Y}_y\text{Ni}_z) = E(\text{Mg}_x\text{Y}_y\text{Ni}_z) - xE(\text{Mg}) - yE(\text{Y}) - zE(\text{Ni}) \quad (2)$$

where $E(\text{Mg}_x\text{Y}_y\text{Ni}_z)$ refers to the total energy of substituted Mg_2Ni by Y.

$E(\text{Mg})$, $E(\text{Y})$ and $E(\text{Ni})$ are the energy of every atom in HCP Mg, HCP Y and FCC Ni crystals, respectively. x , y , z are the numbers of Mg, Y and Ni atoms, respectively. Through the calculation, the values of $E(\text{Mg})$, $E(\text{Y})$ and $E(\text{Ni})$ are -1.595 , -6.379 and -5.415 eV, respectively.

Table 1 displays the volume, lattice constant, total energy and enthalpies of formation of all the structures including Mg_2Ni , substituted Mg_2Ni by Y and their hydrides. The lattice constants of Mg_2Ni after geometry optimization are $a = b = 5.180$ Å, $c = 13.232$ Å, which agree well with the experimental data $a = b = 5.205$ Å, $c = 13.236$ Å [21]. The enthalpy of formation of Mg_2Ni is -3.211 eV, which means that the unit cell of Mg_2Ni is -51.612 kJ/mol. It is very close to the experimental values -51.9 kJ/mol [33]. When Y atom is added into Mg_2Ni , all the volumes of crystal structures will increase compared with the original structures. Moreover, it can be clearly observed that when the position of Mg (6f) is occupied by Y atom in Mg_2Ni , the total energy and the enthalpy of formation are the minimum. It indicates that the structure of $\text{Mg}_{11}\text{Y}(6f)\text{Ni}_6$ has the optimal stabilization among all the substituted structures.

Table 1. Volume, lattice constant, total energy, enthalpy of formation of Mg₂Ni, Y-substituted Mg₂Ni and their hydrides.

Alloy model	Volume (Å ³)	Lattice constant (Å)			Total energy (eV)	Enthalpy of formation (eV)
		<i>a</i>	<i>b</i>	<i>c</i>		
Mg ₂ Ni(exp.) [21]	310.55	5.205	5.205	13.236	—	—
Mg ₂ Ni(cal.)	307.43	5.180	5.180	13.232	-54.836	-3.211
Mg ₂ NiH ₄ (exp.) [23]	545.91	14.343	6.404	6.483	—	—
Mg ₂ NiH ₄ (cal.)	534.63	14.234	6.352	6.434	-192.248	-0.670
Mg ₁₁ Y(6f)Ni ₆	316.88	5.222	5.193	13.437	-59.975	-3.565
Mg ₁₁ Y(6i)Ni ₆	317.74	5.263	5.239	13.328	-59.954	-3.544
Mg ₁₂ Y(3b)Ni ₅	341.89	5.135	5.266	14.481	-53.511	-0.921
Mg ₁₂ Y(3d)Ni ₅	341.23	5.130	5.253	14.510	-53.730	-1.140
Mg ₁₅ YNi ₈ H ₃₂	543.75	14.303	6.396	6.478	-197.148	-0.649

3.2. The Properties of Substituted Mg₂NiH₄ by Y

Based on the stable structure of Mg₁₁Y(6f)Ni₆, we study the properties of substituted Mg₂NiH₄ by Y. Firstly, We have proved that the theoretical lattice constants and internal atomic positions of Mg₂NiH₄ are in good agreement with experimental results [23]. The states are displayed in Table 1. Various substitutive positions of Mg are considered. We find that the total energy of each new structure is very close. Thereby, a reasonable structure Mg₁₅YNi₈H₃₂ is selected to be investigated in detail, as shown in Figure 1(c).

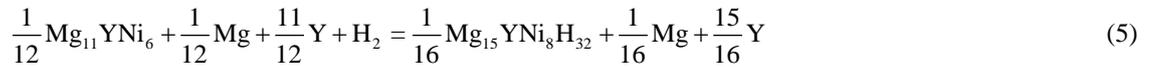
In order to research the effects of Y on the properties of Mg₂NiH₄, We calculate the enthalpies of formation of Mg₂NiH₄ and Mg₁₅YNi₈H₃₂ respectively. In general, the formation of Mg₂NiH₄ can be expressed by the following reaction:



The enthalpy of formation of Mg₂NiH₄ can be expressed in Equation (4):

$$\Delta H(\text{Mg}_{16}\text{Ni}_8\text{H}_{32}) = \frac{1}{16}E(\text{Mg}_{16}\text{Ni}_8\text{H}_{32}) - \frac{1}{12}E(\text{Mg}_{12}\text{Ni}_6) - E(\text{H}_2) \quad (4)$$

In the same way, the reaction of formation and the enthalpy of formation of Mg₁₅YNi₈H₃₂ can be respectively written as Equations (5) and (6):



$$\Delta H(\text{Mg}_{15}\text{YNi}_8\text{H}_{32}) = \frac{1}{16}E(\text{Mg}_{15}\text{YNi}_8\text{H}_{32}) + \frac{1}{48}E(\text{Y}) - \frac{1}{12}E(\text{Mg}_{11}\text{YNi}_6) - \frac{1}{48}E(\text{Mg}) - E(\text{H}_2) \quad (6)$$

where $E(\text{Mg}_{16}\text{Ni}_8\text{H}_{32})$, $E(\text{Mg}_{12}\text{Ni}_6)$, $E(\text{Mg}_{15}\text{YNi}_8\text{H}_{32})$ and $E(\text{Mg}_{11}\text{YNi}_6)$ are the total energy of Mg₂NiH₄, Mg₂Ni, Mg₁₅YNi₈H₃₂ and Mg₁₁Y(6f)Ni₆, respectively.

$E(\text{H}_2)$ is the energy of free H₂ molecule. The calculated results are also shown in Table 1. For pure Mg₂NiH₄, the enthalpy of formation is -64.667 kJ/mol which coincides closely with the experimental result -64.4 ± 4.2 kJ/mol reported by Reilly *et al.* [22]. Furthermore, the enthalpy of formation of Mg₁₅YNi₈H₃₂ is -62.554 kJ/mol which is higher than that of pure Mg₂NiH₄. It can be clearly seen that the introduction of Y atom has effects on the destabilization of Mg₂NiH₄ in terms of energy. This is energetically favorable to perform the dehydrogenation reaction of substituted Mg₂NiH₄ by Y.

To make further investigation about the performance of dehydrogenation, we calculate the energies of Mg₂NiH₄ and Mg₁₅YNi₈H₃₂ which dissociate the nearest 2 H atoms around Ni atoms. The dehydrogenation energy is calculated by Equation (7):

$$\Delta E = E(\text{Mg}_{15}M\text{Ni}_8\text{H}_{30}) - E(\text{Mg}_{15}M\text{Ni}_8\text{H}_{32}) + E(\text{H}_2), (M = \text{Mg}, \text{Y}) \quad (7)$$

The results are shown in **Table 2**. From **Table 2** we can see that the addition of Y clearly decreases the dehydrogenation energy of Mg_2NiH_4 by about 47% to 0.983 eV. It suggests that although Y atom has poor effects on the destabilization of Mg_2Ni , it breaks down the stability of Mg_2NiH_4 positively and improve the dehydrogenation kinetics of Mg_2NiH_4 which as one of the hydrogen storage materials.

3.3. Electronic Structure

In order to further understand the effects of Y atom on the dehydrogenation properties of Mg_2NiH_4 alloy, the electronic properties of Mg_2Ni and $\text{Mg}_{15}\text{YNi}_8\text{H}_{32}$ are studied by calculating total density of states (DOS) and partial density of states (PDOS). **Figure 2** displays the DOS and PDOS of Mg_2Ni and $\text{Mg}_{15}\text{YNi}_8\text{H}_{32}$ alloys.

Form **Figure 2(a)** we can see that there are two main peaks in total density of states below Fermi level. The bonding electron of the energy region between -9.2 and -3.7 eV is mainly dominated by Hs, Nis and Nid orbits, partial Mgs orbit. It is implied that H atoms tend to bond with Ni rather than Mg atoms in the structure of Mg_2NiH_4 . The result is in correspondence with the conclusion that the interaction Ni-H is stronger than that of Mg-H which studied by Jasen [34]. There is a major contribution with Ni *p*, Ni *d* and Mg *s* orbits in the region from -2.4 eV to Fermi level. This indicates that Mg and Ni atoms have hybridization which keeps the structure of Mg_2NiH_4 stable. In addition, Ni *d* orbit plays the dominating role in the bonding electron.

Table 2. Calculated dehydrogenation energies of $\text{Mg}_{15}M\text{Ni}_8\text{H}_{32}$ ($M = \text{Mg}, \text{Y}$) (eV).

M	$E(\text{Mg}_{15}M\text{Ni}_8\text{H}_{32})$	$E(\text{Mg}_{15}M\text{Ni}_8\text{H}_{30})$	ΔE
Mg	-192.248	-183.617	1.856
Y	-197.148	-189.390	0.983

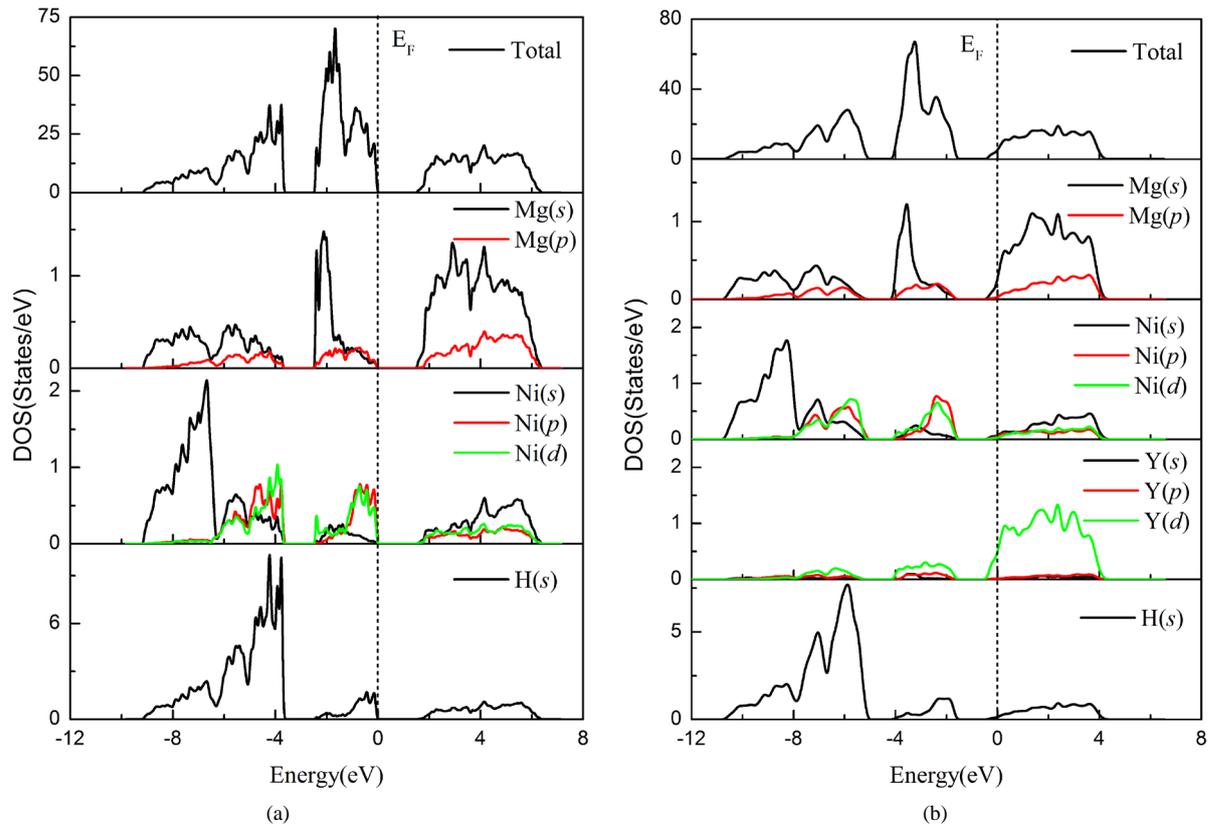


Figure 2. Total density of states and partial density of states of (a) Mg_2NiH_4 , (b) $\text{Mg}_{15}\text{YNi}_8\text{H}_{32}$.

Compared to pure Mg_2NiH_4 , the enthalpy of formation and dehydrogenation energy change markedly due to the substituted Mg_2NiH_4 by Y. **Figure 2(b)** displays that below Fermi level $\text{Mg}_{15}\text{YNi}_8\text{H}_{32}$ has two main bonding peaks from -10.7 to -5.2 eV and -4.1 to -1.6 eV. It is not difficult to find that all the bonding peaks in total density of states move to the energy of deep potential well and the number of bonding electron reduces comparing to Mg_2NiH_4 . It demonstrates that the substitution of Y alloying weakens the interaction of the atoms and destabilizes the structure of the hydride. The effects of Yd orbit on the bonding electron are significant especially for the energy region from -4.1 to -1.6 eV. What is more, Yp and d orbits contribute to the bonding electron and have mutual interaction with Nip and d orbits. It is also worth noting that the overlapping region between Nid and Hs orbits decreases obviously. It means that the interaction between Ni and H atoms become weak.

4. Conclusion

We have investigated the structure and properties of substituted Mg_2Ni alloys by Y and the corresponding hydrides. The structure parameter, enthalpy of formation, dehydrogenation energy and electronic structure are calculated by the first-principles method based on density functional theory in this paper. Through analyzing the simulation results, we can draw the conclusions that when Y atom occupies the Mg(6f) lattice site, the structure of Mg_2Ni is the optimal stable. The substitution of Y destabilizes the stability of Mg_2NiH_4 and decreases the dissociated energies of H atoms due to the Ni-H bond weakened by Y. Therefore, the method of substitution is in favor of the dehydrogenation reaction for Mg-based hydrides as hydrogen storage materials. Moreover, we will continue to perfect this respect, for instance, whether the effect of Y elements in the case of different numbers of Y metals and different substituents will change.

Acknowledgements

This work was supported by Innovation Program of Shanghai Municipal Education Commission, China (10YZ172) and Subjects Construction Program of Shanghai University of Engineering Science, China (2012gp43) and Graduated Innovative Research Project of Shanghai University of Engineering Science (E1-0903-14-01107-14KY0411).

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