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Advanced study of hydrogen storage by substitutional doping of Mn and Ti in Mg$_2$Ni phase

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Abstract – The substitutional doping of Mn and Ti in Mg$_2$Ni phase has been investigated by first principles density functional theory calculations. The calculation of enthalpy of formation shows that among the four different lattice sites of Mg(6f), Mg(6i), Ni(3b) and Ni(3d) in Mg$_2$Ni unit cell, the most preferable site of substitution of Mn in Mg$_2$Ni lattice has been confirmed to be Mg(6i) lattice site. The most preferable site of Ti substitution in Mg$_2$Ni lattice is Mg(6i) position and the stability of Ti-doped Mg$_2$Ni decreases with the increase of substitution quantity of Ti for Mg.

Key words: First principles calculation, Mn-doped Mg$_2$Ni, Ti-doped Mg$_2$Ni, Enthalpy of formation.

1 Introduction

Mg$_2$Ni is considered to be one of the most promising hydrogen storage alloys, because of its lightweight, low cost and high theoretical gravimetric hydrogen storage capacity (3.6 mass%, assuming the formation of Mg$_2$NiH$_4$). Besides, it can absorb and desorb hydrogen at moderate temperatures and pressures. However, the poor hydriding/dehydriding kinetics and high thermodynamical stability of Mg$_2$NiH$_4$ (requiring 280 °C for 1 bar hydrogen [1]) become the obstacle for the practical use for hydrogen storage. Mn [2, 3] and Ti [4] have been experimentally added into Mg$_2$Ni for improving its hydrogen storage properties.

The unit cell of Mg$_2$Ni contains two symmetry-inequivalent types of Mg atoms, namely Mg(6f) and Mg(6i), and two types of Ni atoms, viz Ni(3b) and Ni(3d) [5]. Therefore, there exist four possible substitution sites for Mn and Ti in Mg$_2$Ni lattice. However, to the best of our knowledge, the studies on which position is the most preferable site for Mn and Ti substitutions among Mg(6f), Mg(6i), Ni(3b) and Ni(3d) in Mg$_2$Ni lattice are lacked.

In this work, we study the substitutional doping of Mn and Ti in Mg$_2$Ni phase by first principles density functional theory calculations. The preferable sites of substitutions of Mn and Ti in Mg$_2$Ni lattice have been determined by total energy

calculation, which provides a guide for using the method of elemental substitution to improve the hydrogen storage properties of Mg$_2$Ni intermetallic compound.

2 Computational models and method

The unit cell of Mg$_2$Ni phase belongs to the space group $P6_222$ with lattice parameters $a = 5.216(6)$ Å, $c = 13.20(6)$ Å [5]. Each unit cell contains six formula units and thus it can be expressed as Mg$_{12}$Ni$_6$. The 12 Mg atoms occupy Mg(6f) and Mg(6i) lattice sites, while six Ni atoms occupy Ni(3b) and Ni(3d) lattice sites. To investigate the effects of substitutional doping, a Mn or a Ti atom was introduced into the Mg$_2$Ni unit cell to substitute the atoms at Mg(6f), Mg(6i), Ni(3b) and Ni(3d) lattice sites, respectively.

The calculation in this work has been carried out using the CASTEP programme [6], which is a first principles quantum mechanical code based on the density functional theory. It employs plane-wave basis sets to treat valence electrons and pseudopotentials to approximate the potential field of ionic cores (including nuclei and tightly bond core electrons) [7]. The Perdew-Burke-Ernzerhof (PBE) [8] generalized gradient approximation (GGA) exchange and correlation potential was used in the calculations. Ultrasoft pseudopotentials [7] in reciprocal space were used to replace the core electrons. The special points sampling integration over the Brillouin zone was carried out by using the Monkhorst-Pack method [9]. We have

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Table 1. Experimental and calculated structural parameters of Mg_2Ni.

Compound		Lattice constants (Å)		Atom site	Fractional coordinates					
		Experimental	Calculated		Experimental			Calculated		
Mg_2Ni ($P6_222$)	a	5.216(6) [5]	5.218	Mg(6f)	0.5	0	0.1149(2) [5]	0.5	0	0.1163
	c	13.20(6)	13.246	Mg(6i)	0.1635(6)	0.327	0	0.1642	0.3284	0
				Ni(3b)	0	0	0.5	0	0	0.5
				Ni(3d)	0.5	0	0.5	0.5	0	0.5

The digits in parentheses for experimental lattice constants and fractional coordinates are standard deviations.

tested the dependence of the total energy on the cutoff energy values and the k-point sets.

For Mg_2Ni unit cell, when the cutoff energy is higher than 380 eV and the k-point sets are beyond $6 \times 6 \times 2$, the change in total energy is less than 1.64 meV/atom. In consideration of computational cost, the geometry optimization calculations were performed with a cutoff energy of 380 eV and a k-point mesh of $6 \times 6 \times 2$ for pure and Mn or Ti-doped Mg_2Ni unit cell. The convergence criteria were set at 5.0×10^{-6} eV/atom for energy change, 0.01 eV/Å for maximum force, 0.02 GPa for maximum stress and 5.0×10^{-4} Å for maximum displacement.

The enthalpy of formation of a compound can be defined as the difference between its total energy and the energies of its constituent elements in their stable states (referred to the elementary substances). The zero-point energy (ZPE) contributions are significant in reactions where hydrogen molecules are adsorbed or desorbed [10]. We focus on the reactions that only contain alloys (without hydrogen) in this work. Thus, the ZPE contributions are not considered in this study. Therefore, for a lattice containing x Mg atoms, y M (Mn or Ti) atoms and z Ni atoms, the enthalpy of formation per unit cell is given by:

$$\Delta H_f = E_{tot}(Mg_x M_y Ni_z) - [xE(Mg) + yE(M) + zE(Ni)] \tag{1}$$

where ΔH_f and E_{tot} refer to the enthalpy of formation and total energy per unit cell of the compound, respectively. $E(Mg)$ and $E(Ni)$ are the single atomic energies of the hcp-Mg and fcc-Ni in the solid state, respectively. $E(M)$ is the single atomic energies of the α-Mn or hcp-Ti in the solid state. The enthalpy of formation can be used to demonstrate whether and how much a compound structure is favored over its constituent elements in thermodynamics.

3 Results and discussion

3.1 Mn-doped Mg_2Ni

At first, the calculation of Mg_2Ni crystal was performed with full optimization of both the lattice parameters and the coordinates of all atoms based on the experimentally confirmed structure. The calculated values are listed in Table 1 and compared with the experimental data. This table shows that the difference between calculated and experimental values is below 1.3% for all results, which indicates that present calculations are in good agreement with the experimental results. As shown

Table 2. Total energy and enthalpy of formation of calculated Mn-doped models.

	Total energy (eV)	Enthalpy of formation (eV)	
	Unit cell	Unit cell	Per atom
Mg_2Ni	−19817.2794	−3.2691	−0.1816
$Mg_{11}Mn_{Mg(6f)}Ni_6$	−19496.4273	−2.7273	−0.1515
$Mg_{11}Mn_{Mg(6i)}Ni_6$	−19496.4777	−2.7777	−0.1543
$Mg_{12}Mn_{Ni(3b)}Ni_5$	−19115.3243	−2.1059	−0.1170
$Mg_{12}Mn_{Ni(3d)}Ni_5$	−19115.3679	−2.1495	−0.1194

in Table 2, the calculated enthalpy of formation of Mg_2Ni unit cell is −3.2691 eV, which can be transferred into −52.57 kJ/mol Mg_2Ni formula unit. This value is close to −51.9 kJ/mol reported in reference [11]. Therefore, our calculations are reliable.

In order to study the effects of substitutional doping of Mn in Mg_2Ni phase, a Mn atom is added into Mg_2Ni unit cell to substitute a Mg (or Ni) atom at the positions 6f and 6i (or 3b and 3d), respectively. As shown in Table 2, the chemical formulae of the Mn-doped Mg_2Ni unit cells are expressed as $Mg_{11}Mn_{Mg(6f)}Ni_6$, $Mg_{11}Mn_{Mg(6i)}Ni_6$, $Mg_{12}Mn_{Ni(3b)}Ni_5$ and $Mg_{12}Mn_{Ni(3d)}Ni_5$, respectively. The enthalpy of formation is fundamental for evaluating the structural stability.

The calculated enthalpies of formation per unit cell of the pure and Mn-doped Mg_2Ni unit cell are also tabulated in Table 2. It can be obtained that Mg_2Ni has the most negative enthalpy of formation, indicating that it is the most stable structure in thermodynamics. However, the Mn substitutions for Mg or Ni atom in Mg_2Ni phase decrease the stability of Mg_2Ni phase because of the less negative enthalpies of formation in comparison with pure Mg_2Ni phase. We have reported that during the mechanical alloying of elemental powders of Mg, Ni and Mn, the first appearing phase was Mg_2Ni and it was difficult for Mn to substitute Ni site in Mg_2Ni lattice structure [12].

The present calculated enthalpy of formation shows that pure Mg_2Ni phase is more favored in thermodynamics than the Mn-dope phases, which is in good agreement with the phenomenon found in reference [12]. In addition, the enthalpies of formation of $Mg_{11}Mn_{Mg(6f)}Ni_6$ and $Mg_{11}Mn_{Mg(6i)}Ni_6$ are −2.7273 eV and −2.7777 eV, respectively, both of which are more negative than those of $Mg_{12}Mn_{Ni(3b)}Ni_5$ (−2.1059 eV) and $Mg_{12}Mn_{Ni(3d)}Ni_5$ (−2.1495 eV). Therefore, the Mn atom prefers to substitute Mg in Mg_2Ni lattice in comparison with Ni. Furthermore, between Mg(6f) and Mg(6i) lattice sites, it is more favorable for Mn atom to replace the Mg(6i) position
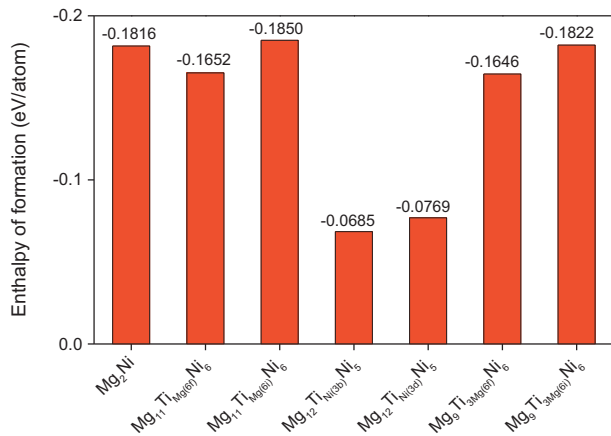
Figure 1. Enthalpies of formation of calculated Ti-doped models.

due to the most negative enthalpy of formation of -2.7777 eV for $Mg_{11}Mn_{Mg(6i)}Ni_6$ among the four Mn-doped phases. As a result, the calculated enthalpy of formation confirms that the most preferable site of substitution of Mn in Mg_2Ni lattice is Mg(6i) position. This can provide a guide for using the method of elemental substitution to improve the hydrogen storage properties of Mg_2Ni intermetallic compound. Takahashi et al. [13] reported that both the Ni-H and the Ni-Mg atomic interactions were found to affect directly the phase stability of the hydride.

As mentioned above, the Mn substitutions for Mg or Ni atom in Mg_2Ni phase decrease the stability of Mg_2Ni phase, which indicates that the Ni-Mg atomic interactions are weakened. Therefore, Mn substitutions for Mg or Ni atom in Mg_2Ni phase are probably favorable for decreasing the stability of the hydride. Yang et al. [14] found that replacement of Ni in Mg_2Ni by Mn lowered the decomposition plateau pressure. Jurczyk et al. [15] obtained an enhanced discharge capacity by substituting Mg with Mn in Mg_2Ni alloy. Kohno and Kanda [2] reported that as a result of substitution of Mg with Mn, absorption of hydrogen occurred at lower temperature, which indicates that substituting Mg with Mn can overcome the poor hydriding/dehydriding performance of Mg_2Ni alloy. As a result, the hydrogen storage properties can be tailored by appropriate designing of Mn substitution.

3.2 Ti-doped Mg_2Ni

The calculated enthalpies of formation of all calculated Ti-doped models are shown in Figure 1. For the sake of studying the effects of substitutional doping of Ti in Mg_2Ni phase, a Ti atom is added into Mg_2Ni unit cell to substitute the metal atom at the positions Mg(6f), Mg(6i), Ni(3b) or Ni(3d), respectively. As shown in Figure 1, the chemical formulas of the corresponding Ti-doped Mg_2Ni unit cells are expressed as $Mg_{11}Ti_{Mg(6f)}Ni_6$, $Mg_{11}Ti_{Mg(6i)}Ni_6$, $Mg_{12}Ti_{Ni(3b)}Ni_5$ and $Mg_{12}Ti_{Ni(3d)}Ni_5$, respectively. As can be seen in Figure 1, the Ti substitutions for Ni atoms at Ni(3b) and Ni(3d) sites in Mg_2Ni phase decrease the stability of Mg_2Ni phase because of the less negative enthalpies of formation of $Mg_{12}Ti_{Ni(3b)}Ni_5$ and $Mg_{12}Ti_{Ni(3d)}Ni_5$ in comparison with that of pure Mg_2Ni phase.

The Ti substitution for Mg atom at Mg(6f) site also destabilizes the Mg_2Ni unit cell, but in contrast the Ti substitution for Mg atom at Mg(6i) site stabilizes the Mg_2Ni unit cell. Therefore, according to Figure 1, it can be concluded that the Ti atom prefers to substitute Mg in Mg_2Ni lattice in comparison with Ni. Furthermore, between Mg(6f) and Mg(6i) lattice sites, it is more favorable for Ti atom to replace the Mg(6i) position due to the most negative enthalpy of formation of -0.1850 eV/atom for $Mg_{11}Ti_{Mg(6i)}Ni_6$ among the four Ti-doped phases. As a result, the calculated enthalpies of formation confirm that the most preferable site of substitution of Ti in Mg_2Ni lattice is Mg(6i) position. By using three Ti atoms to substitute three Mg atoms at Mg(6i) position (the most preferable site of substitution of Ti) in the Mg_2Ni unit cell, $Mg_9Ti_{3Mg(6i)}Ni_6$ is obtained. For comparison, the enthalpy of formation of $Mg_9Ti_{3Mg(6f)}Ni_6$ has also been calculated. By comparing the enthalpies of formation of $Mg_9Ti_{3Mg(6i)}Ni_6$ and $Mg_9Ti_{3Mg(6f)}Ni_6$ with those of $Mg_{11}Ti_{Mg(6i)}Ni_6$ and $Mg_{11}Ti_{Mg(6f)}Ni_6$, respectively, we could conclude that the stability of Ti-doped Mg_2Ni decreases with the increase of substitution quantity of Ti for Mg. For example, the calculated enthalpy of formation of $Mg_9Ti_{3\,Mg(6i)}Ni_6$ is -0.1822 eV/atom, which is less negative than that (-0.1850 eV/atom) of $Mg_{11}Ti_{Mg(6i)}Ni_6$.

4 Conclusions

The substitutional doping of Mn and Ti in Mg_2Ni phase has been investigated by first principles density functional theory calculations. Based on this study, the following conclusions can be obtained: (1) The calculated lattice parameters and atomic coordinates are in good agreement with the experimental results. The calculation of enthalpy of formation shows that pure Mg_2Ni phase is more favored in thermodynamics than the Mn-dope phases. The possibility of the site of Mn-substitution in Mg_2Ni lattice has been confirmed to be Mg(6i) > Mg(6f) > Ni(3d) > Ni(3b) positions. (2) The most preferable site of Ti substitution in Mg_2Ni lattice is Mg(6i) position and the stability of Ti-doped Mg_2Ni decreases with the increase of substitution quantity of Ti for Mg.

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