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Thermal Stability of the Mg_2Ni-Based Hydrogen Storage Alloy Doped Ti Element

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ABSTRACT

Crystal structures, electronic structures, thermal stability and dehydrogenation energy of Mg-based hydrogen storage materials were investigated via the first-principle calculations, and the calculations of bonding properties, electronic structure, band structure, density of state, charge density difference and electronic structure of Mg_2Ni alloy were examined. Namely, the work mainly took account of doping metal elements Ti to replace Mg and Ni elements in different proportions portion, and then form different crystals, including $Mg_{12}Ni_6$, $Mg_{1.5}NiTi_{Mg(2)1/2}$, $Mg_{5/3}NiTi_{Mg(2)1/3}$, Mg_2NiH_4, $Mg_2Ni_{3/4}Ti_{1/4}H_4$ aimed to improve the hydrogen storage characteristics of Mg-based metal hydrides. The results manifested Ti elements may hold the center position of octahedral sites, and the investigation further indicated that the hydrogen release performance and the thermal stability of hydrogen became lower through calculating absorption reaction enthalpy. Additionally, the metals Ti with high electronegativity interstitially exhibit useful effects on the characteristics of Mg-based hydrogen storage, which is beneficial to find the impact of the mechanism in terms of the electronic structure, and provide the theoretical support for designing new hydrogen storage materials.

Keywords: Thermal stability, Magnesium-based, Hydrogen storage, Mg_2Ni doped Ti, First principles.

1. INTRODUCTION

A_2B type magnesium-based (Mg_2X-based) alloys are considered to be promising hydrogen storage materials and exerted a tremendous fascination on us in current years [1], and then become a new application field of magnesium alloys, which due to the incorporation of elements X (X=Al, Ca, Sn, Cu, Co, Fe and Ni, etc.). Noted that Mg-based hydrogen storage alloys are considered to be one of the most valuable metal materials because of its critical characteristics of extremely hydrogen storage capacity and rich natural resources. Especially, it is universally acknowledged that Mg_2Ni-based alloys have a large hydrogen storage capacity of 3.6% mass fraction, and they are up to 999mA·g^{-1} theoretical discharge capacity [2].

Studies advocated it for the first time that the experimental and theoretical research is primarily focused on the thermodynamic properties and phase stability Mg_2X (X=Ni) alloy aspect [3-7]. Although, previous studies demonstrated that the speed hydrogen storage is slow at room temperature, and hydrogen desolation temperature is so high that hydrogen is difficult to store in the aspects of kinetic releasing performance. In addition, Mg_2Ni alloy easily powder during hydrogen absorption and released repeatedly, and cyclic stability is poor, which have already restricted the research and practical applications of Mg_2Ni metal as the hydrogen storage materials [7]. In order to increase their hydrogen absorption and desolation kinetics performance and stability, for instance, hydrogen absorption velocity and temperature of hydrogen released of magnesium-based alloy.

Recently, the work of doping metals into Mg-based metal hydrides was increasingly investigated to improve the hydrogen storage characteristics, because Ti metals have better effects on improving the characteristics than transition metals. $Mg_{1.5}Ti_{0.5}Ni$ alloy milled for 20h showed the highest discharge capacity among all milled alloys [8]. Literatures reported Reill and Wiswall first mixed magnesium and nickel alloy and obtained Mg_2Ni, and the hydrogen-absorbing alloy was considered as a good prospect secondary battery anode material. Imamura et al. [9] reported that the performance of the new charge and discharge of hydrogen composite hydrogen storage materials were improved with a magnesium-based material doped Fe, Ni and other elements. Orimoi et al. [10] produced a large volume of disordered grain boundaries among the grain boundary region of Mg_2Ni alloy on the condition of mechanical milling, not only increased the hydrogen storage capacity, but also remain the overall structure of nanocrystals same. Additionally, a large number of theoretical studies discovered that it is useful for Mg_2Ni alloy to improve hydrogen storage properties accompanied by the amorphous of disordered grain boundary [11-12]. In addition, Kohn et al. [13] found that Mg_2Ni exhibit superior hydrogen absorption properties due to its nanocrystalline structure.

However, poor hydride-dehydride kinetic is fiancially-challenged at room temperature, thereby a few of reports further demonstrated that magnesium nickel hydrogen storage alloys exist some defects of poor performance and poor cycle stability in hydrogen absorption and desorption kinetics. Therefore, theoretical calculations [14, 15] revealed the desorption mechanism, and could predict the structure and properties of Mg_2Ni hydrogen storage alloy. Afterwards, experimental study [16-18] showed that other elements doped into the alloy structure of Mg_2Ni could improve hydrogen storage properties to a certain extent, however, which only enhanced the dynamic properties of the alloy, rather than thermodynamic performance. More recent studies by Literature [19] reported that the hydrogen reacted with Mg_2Ni when the crystal structure changed hydride, and the key was to substitute or incorporate Ti element and then change the structure of magnesium-based material during hydride hydrogen absorption and desorption to reduce thermal effects. Moreover, Myers et al. calculated the crystal structure of Mg_2NiH_4 with low-temperature phase, and analyzed its enthalpy heat generating electronic structure and optical properties. Alapati et al. [20, 14, 15] calculated chemical reaction enthalpy of metal hydride and derived Van't Hoff relationship about the pressure and temperature of hydrogen by first-principles. Afterwards, García et al. [21, 22] calculated the crystal structure and electron distribution the of Mg_2NiH_4 with high temperature phase, and also discussed the hydrogen atoms' position among the high temperature phase and speculated the bond type between each atom of hydrogen storage alloys [23-26].

From abovementioned, quintessential reports addressed the progress on magnesium-based storage alloy. Partial elements substitution have been proved to improve electrochemical properties of Mg_2Ni-based alloys [27]. Furthermore, the advantages hydrogen storage alloys, especially the basic research on Mg_2Ni-based hydrogen and disadvantages of the hydrogen storage alloys are reviewed. Additionally, the means of improving surface structures of Mg_2Ni hydrogen storage alloy and other compound elements are summarized, and then put forward the method what elemental substitution [28-31] can effectively reduce the enthalpy of formation reaction. However, little achievement focused on Ni metal elements doped into Mg-based metal hydrides, namely effect of hydrogen absorption and desorption properties by doping the high electronegativity elements additives with the weakening of the strong interaction of Mg H and Ni H atoms was relatively scarce. In view of Mg_2NiH_4 with the low-temperature phase, there were two aspects of this problem have to be addressed, the first question involved that the Ti atom is substituted to form the new phases based on density functional theory (DFT) via the first-principles calculation, including Ti doped with different proportions portion $Mg_{2-x}Ti_xNi$ (x=0, 1/6, 1/3) of Mg and Ni alloy elements on the structural stability Mg_2NiH_4. The second aspect related to investigate systematically the hydrogen effect of absorption and desorption properties on Mg_2NiH_4 and Mg_2Ni throughout the calculation of the density of states, charge density difference, crystal structure, electronic structure and bonding characteristics. Accordingly, the study further deal with reaction enthalpy changes of hydrogen absorption to reduce the thermodynamic stability of Mg_2Ni alloy and to improve the hydrogen release performance, which should beneficially find the impact of the mechanism in terms of the electronic structure, and to provide new ideas and theoretical basis for the new hydrogen storage materials.

2. METHOD OF CALCULATIONS

Quite a few of studies demonstrated that atomic structure of Mg_2Ni belongs to hcp layered structure [32], and its crystal structures and hydride may be doped with a certain number of Ti elements to form new phases. Generally, its space groups are $P6_222$ (No. 180) and monoclinic C2/c, the lattice constants are a=0.5205nm, c=1.3236nm, $\alpha=\beta=90°$, and $\gamma=120°$ [33, 34], and the unit cell model is highly symmetrical D6-4, including six face which are parallel to the XY plane, and each primitive cell has twenty Mg atoms and six Ni atoms, as shown in Fig.1, these atoms constitute one new cell, we named it as $Mg_{12}Ni_6$. Wherein Mg atom is positioned 6f (0.5, 0, 0.1187) and 6i (0.162, 0.324, 0), and the position of the Ni atom is 3b (0, 0, 0.5) and 3d (0.5, 0, 0.5).

In this work, periodic boundary conditions are used to calculate with CASTEP (Cambridge serial total energy package) [36], and the exchange-correlation part is described with GGA (Generalized Gradient Approximation) exchange-correlation function developed by Perdew, Burke and Ernzerh (PEB) [36, 37], and the appropriate parameters including density approximation function and plane wave basis set extensions in the framework of Ultrasoft [38], which were be beneficial to set the wave function and describe the interaction of electrons and ions. In addition, the lattice parameters and the atomic position are fully relaxed, and calculations were based on the test the convergence of a few important parameters by the first-principle when $E_{cut\text{-}off}$ of the plane waves was 350 eV, and then to optimize structural model and provide the most stable state of Mg_2Ni structure and energy. Moreover, the method of Monkhors-Pack was used in the simple Brillouin zone during self-consistent iterative process [39], and convergence indicators of structural optimization were executed in the following parameters. In addition, interatomic force is less than 0.05 eV/Å, and the force on each atom is less than 0.03 eV·Å, and maximum force of each relaxed atom is lower than 1×10^{-5} eV·atom^{-1}. Respectively, internal stress is less than 0.05 GPa, and self-consistent accuracy is 1.0×10^{-6} eV·atom^{-1}, and the tolerance offset is less than 0.00l Å.

3. RESULTS AND DISCUSSION

To investigate the effect of substitutional doping, the exam has tested the total energy on the Ecut-off and K-point (6×6×2), and then optimized crystal structure of Mg_2Ni unit cell and its hydrides, and also calculated the energy of alloy cell when adding Ti element. Afterwards, crystal structures, electronic structures, thermal stability and dehydrogenation energy of mg-based hydrogen storage materials were calculated, respectively, the calculations of bonding properties, electronic structure, band structure, density of state, charge density difference and electronic structure of Mg_2Ni alloy was examined. Namely, the experiments mainly took account of doping metal elements Ti to replace Mg and Ni elements in different proportions portion, and then form different crystals model by using one Ti-atom instead of three Ni atoms of $Mg_{12}Ni_6$ unit cell, and the electronic structure model shown in Fig.1.

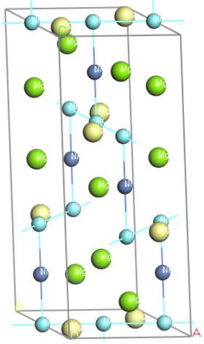

Figure 1. Structural modle of Mg_2Ni

Table 1. Cell parameters of Mg alloys [32]

parameters	$Mg_{12}Ni_6$ (cal.)	$Mg_{12}Ni_6$ (exp.)	$Mg_{12}Ni_3Ti_3$ (cal.)
a(Å)	5.217	5.205	5.284
b(Å)	5.217	5.2105	5.284
c(Å)	13.289	13.236	15.012
Volume(Å^3)	317.443	310.548	363.995

Consequently, structural optimization results of $Mg_{12}Ni_6$ and $Mg_{12}Ni_3Ti_3$ cell are shown in Tab.1. It displays the lattices constant and volume of the primitive cell, and also can be obviously observed that the calculation of the parameters and conditions selected are rational. Similarly, the test results show that the equilibrium lattice constants of Mg_2Ni (a=b=5.217Å, c=13.289Å) and Mg_3TiNi_2 agrees well with experimental values, and the error is only 0.27% and 0.53%. Furthermore, the results indicated that the lattice constant of the solid solution is changed because of doping Ti element, and the problem of decrescent volume of unit cell arises in part from the shorter bond between Ti and Mg, Ni atom.

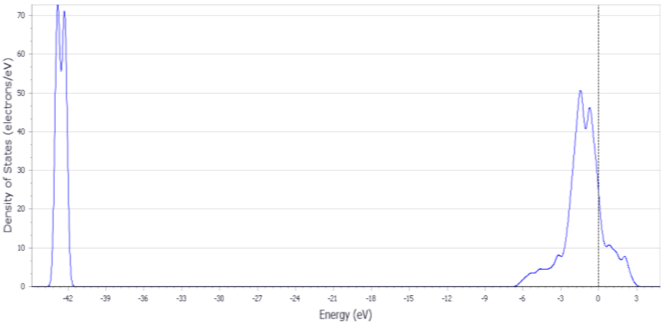

Figure 2. Total DOS of Mg_2Ni doped Ti

Fig.2 is the total density of states of Mg_2Ni doped with Ti element. It can be seen that DOS of Mg_2Ni system is mainly distributed in the energy range of -7~3eV, and found that DOS is nonzero when crossing the fermi level, which means that the alloy has a very obvious metallic. The calculation results also state that the interaction between atoms occurs mainly in the vicinity of Ni atomic layer, and atomic interactions between Mg and Ni atoms along the c-axis are weak. By contrast, the interaction along a, b-axis is stronger than along the c-axis between atoms.

In Fig.3, the exam can be derived conclusions in consideration of investigating the region of substitution surroundings and others. Consequently, the total density of states is greatly reduced when Ti element substituted Ni atom, and the density under fermi level is higher than the single substance, especially relative proportion is much higher, which suggests the stability of Ti element is improved after doping atoms. However, the total density of states of the conduction band is reduced, and total DOS above the fermi level increase, which means cell stability and desorption temperature changes lower, and the hydrogen storage properties are improved. Additionally, the charge density distribution shows clearly the interaction and electron distribution, which indicates that the electrons of Mg atoms don’t transfer into d-orbital of Ni atoms, and there is a certain interaction between these electrons and Ni atoms, hence the conclusion is consistent with the density of states.

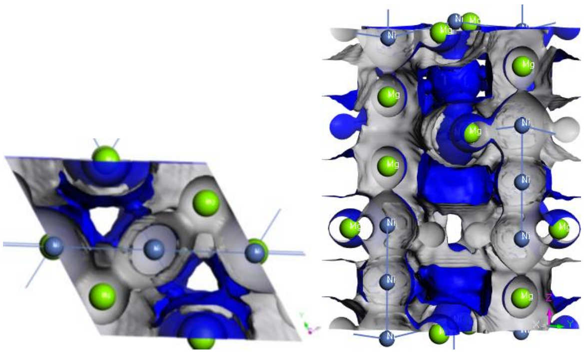

Figure 3. Total DOS of Mg_2Ni doped Ti

Subsequently, the work calculated the stability of Mg_2Ni alloy systems doped Ti atoms in contrast with Mg_3TiNi compounds. Noted that alloy enthalpy is an important indicator to evaluate the stability of the phase structure, this applies to the alloy with the same constituent elements and different structure. Generally, enthalpy is more negative, and the corresponding alloy is more stable. In order to investigate the impact on the stability of Mg_2Ni alloy after Ti-doped, the examine calculated enthalpy of Mg_2Ni and its alloy phase by expression [40], thereby and the stability of Mg_2Ni alloy systems doped Ti with respect to Mg_3TiNi_2 compounds is shown in Tab.2. In this case, $\varDelta H$ is generated to the enthalpy of every kind of hydrogen storage during forming hydride, and it closely related with the stability of the hydrides. This study calculated $\varDelta H$ using the following Eq. (1) [41]:

$$\Delta H = \frac{1}{8}E(Mg_8Ni_3TiH_{16}) - \frac{1}{24}[E(Mg_{12}Ni_6) + E(Mg_{12}Ni_3Ti_3)]\text{-}E(H_2) \tag{1}$$

wherein, one lattice containing Mg, Ti and Ni atoms, and the enthalpy of formation per unit cell are given by the equation. In addition, E represents the total energy of the unit cell when the reaction reaches equilibrium, and $\varDelta H$ represents the enthalpy generated a variety of substances, this reaction belongs to exothermic when $\varDelta H$ value is negative.

The resultant structure is considered to be more stable when the total heat released is more [42], and enthalpy value of alloy doped Ti elements are relatively small (only -52.8 KJ·mol^{-1}), which described that Ti element can reduce the structural stability of Mg_2NiH_4 and then improve performance its releasing hydrogen.

Table 2. The enthalpy of Mg_2Ni and its hydride [43, 44]

Conpound	ΔH ($KJ\cdot mol^{-1}$) (Exp.)	ΔH ($KJ\cdot mol^{-1}$) (Cal.)
$Mg_{12}Ni_6$	-13.00	-11.34
$Mg_{3/2}NiTi_{Mg(2)1/2}$	-	-7.66
$Mg_{5/3}NiTi_{Mg(2)1/3}$	-	-8.03
Mg_2NiH_4	-61.00	-55.70
$Mg_2Ni_{3/4}Ti_{1/4}H_4$	-56.00	-52.80

As a result, when the concentration of doping Ti-atoms is 1/3~1/2, the enthalpies calculation shows that the stability of $Mg_{3/2}NiTi_{Mg(2)1/2}$ solid solution alloy is less than Mg_3TiNi_2 compound with cubic structure, and $Mg_{3/2}NiTi_{Mg(2)1/2}$ can easily transit from a hexagonal structure to a cubic structure on this concentrations. Moreover, calculated value of Mg_2Ni alloy enthalpy is -11.34 $kJ\cdot mol^{-1}$, and it occurs obviously minor differences in comparison with experimental value -13 $kJ\cdot mol^{-1}$, which implies that the difference is probably on the account of temperature. On the other hand, hydrogen reaction enthalpy is TiH > H, which describs that energy released by Mg_3TiNi_2 is less in the case of hydrogen absorption. Namely, the heat energy of dehydrogenation is less than pure Mg_2Ni, as the result, the solution of hydrogen easily occurs. In practice, the results from the quantitative standpoint accounts that the capacity of hydrogen solutions of Mg_2Ni hydride system can be improved by doping Ti.

4. CONCLUSIONS

In summary, the work has systematically calculated crystal structure, lattice constants, band structure and charge density, especially enthalpy of Mg_2Ni and its hydride charge, and further to discuss the thermal stability and dehydrogenation energy of Mg_2Sn and its hydride. The results demonstrated that total DOS of Mg_2Ni system is mainly distributed across the fermi level, which means that the metallic of the alloy is very obvious. Namely, the metal Ti element with high electronegativity is employed to Mg-based hydrogen storage, and its lattice constant of the solid solution is easily changed, and its hydride can easily change from a hexagonal structure to a cubic structure on certain concentration condition. Additionally, partially replace Ti atom can reduce structural stability and then improve the release properties of hydrogen hydride, which is helpful in designing the next generation high-performance thermodynamic materials.

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