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First-principles study on structural stability of 3d transition metal alloying magnesium hydride

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Abstract: A first-principles plane-wave pseudopotential method based on the density functional theory was used to investigate the energy and electronic structure of magnesium hydride (MgH₂) alloyed by 3d transition metal elements. Through calculations of the negative heat formation of magnesium hydride alloyed by X (X denotes 3d transition metal) element, it is found that when a little X (not including Sc) dissolves into magnesium hydride, the structural stability of alloying systems decreases, which indicates that the dehydrogenation properties of MgH₂ can be improved. After comparing the densities of states(DOS) and the charge distribution of MgH₂ with or without X alloying, it is found that the improvement for the dehydrogenation properties of MgH₂ alloyed by X attributes to the fact that the weakened bonding between magnesium and hydrogen is caused by the stronger interactions between X (not including Cu) and hydrogen. The calculation results of the improvement for the dehydrogenation properties of MgH₂ - X (X=Ti, V, Mn, Fe, Co, Ni, Cu) systems are in agreement with the experimental results. Hence, the dehydrogenation properties of MgH₂ are expected to be improved by addition of Cr, Zn alloying elements.

Key words: magnesium hydride; plane-wave pseudopotential theory; heat formation; electronic structure

1 Introduction

Nowadays, many efforts have been spent to develop hydrogen storage materials for non-polluting applications. Magnesium hydrogen systems can act as a thermal energy storage system in the future. Magnesium-based hydrogen storage alloys have been extensively researched due to their high hydrogen storage capacity, light mass and low cost. However, the slow hydriding and dehydrogenating kinetics and high dissociation temperature caused by its relatively high stability limit its practical application for hydrogen storage. The main objective of many current studies has been done to reduce the high Mg-H binding energy by alloying additions, so as to reduce the sorption temperature. Numerous studies have been carried out in order to identify a suitable alloy that absorbs hydrogen close to room temperature and desorbs hydrogen at a temperature low enough to use the waste heat of exhaust gas. Both nanocrystallization and addition of transition metal catalysts demonstrated to improve the hydrogen sorption kinetics of Mg. Recent experiment investigations[1 - 4] have shown that the mechanical alloying of MgH₂ and 3d transition metal elements, for example, Ni, Co, Mn, Cu, Ti, Fe, V, effectively improves the hydriding and dehydrogenating kinetics of MgH₂ at high temperature. As far as 3d transition metal is concerned, Ti and V, when mixed with the magnesium hydrides by ball milling, are better catalysts than Ni for magnesium hydrides. Although Ni is commonly used for hydrogen absorption in Mg and its alloys, it is not a catalyst as good as Ti and V. This has been attributed to the effect of oxygen. Titanium and vanadium have very strong affinities to oxygen, and their oxides can not be reduced by hydrogen under normal conditions. This is the reason why Ni has better catalytic effects than Ti and V in conventional Mg-based alloys. Mechanical milling of MgH₂ with Ti or V leads to titanium or vanadium hydrides, which could protect Ti or V from oxidation, and therefore the catalytic effect towards hydrogen is preserved. To understand the intrinsic mechanisms of 3d transition metal alloying effects on the dehydrogenating properties of magnesium hydride, YONG et al[5], calculated the total energy and the electronic structure of the solution of the 10% (mole fraction) alloying elements such as Fe, Ni, Cu, Ti into

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the magnesium hydride by adopting the full-potential linearized augmented phane-wave method. It is found that the alloving elements are considered to destabilize the magnesium hydride, and hence the dehydrogenation properties of MgH₂ are improved. Based on the previous experimental works which the dehydrogenation properties of MgH₂ can be improved by the addition of 3d transition metal, such as Ni, Co, Mn, Cu, Ti, Fe, V, but there was little effort to understand the intrinsic mechanisms of 3d transition metal for Sc, V, Cr, Mn, Co, Zn. Hence, in this paper, a first-principles plane-wave pseudopotential method based on the density functional theory has been used to investigate the energy and electronic structure of magnesium hydride (MgH₂) alloyed by 3d transition metal elements. Moreover, the structural stability and electronic mechanism of 3d transition metal alloying magnesium hydride were analyzed and discussed, and then, some new results would be given.

2 Method of models of computation

MgH₂ has a tetragonal symmetry (P4₂/mnm, Group No.136). Two Mg atoms occupy (0, 0, 0) site and four H atoms locate in (0.304, 0.304,0) sites (Fig.1 (a)). The lattice parameters are a=0.450 1 nm and c=0.301 0 nm, respectively[6].In this work, we employed a supercell with 5 times in c axis of the unit cell, as shown in Fig.1(b). Due to the symmetry requirement, there are three nonequivalent sites for magnesium and hydrogen atoms in the supercells, as listed in Table 1. To investigate the influence of alloying elements X (X denotes 3d transition metal) on the structural stability, the total energy and electronic structure of magnesium hydrides, two Mg atoms in the supercells are replaced by alloying atoms. Hence, the Mg₈X₂H₂₀ supercells are given.

 Table 1 Structure of supercell used in present calculation

Atom	x	у	-	Number of
			2	atoms
Mg1(X)	0	0	0	2
Mg2	0	0	0.2	4
Mg3	0	0	0.6	4
H1	0.304	0.304	0	4
H3	0.196	0.804	0.1	8
H2	0.304	0.304	0.2	8

Cambridge serial total energy package (CASTEP) [7], a first-principles plane-wave psendopotentials method based on density functional theory, is used in this work. CASTEP uses a plane-wave basis set for the expansion of the single-particle Kohn-Sham wavefunctions, and psendopotentials to describe the computationally expensive electron-iron interaction, in which the exchange-correlation energy by the generalized gradient approximation(GGA) of Perdew is adopted for all elements in our models by adopting Perdew- Burke-Ernzerhof parameters[8]. Ultrasoft represented in reciprocal space is used[9]. In the present calcu- lations, the cutoff energy of atomic wave functions (PWs), E_{cut} , is set at 310 eV. Sampling of the irredu- cible wedge of Brillouin zone is performed with a regular Monkhorst-Pack grid of special k-points, which is $6 \times 6 \times 6$. A finite basis set correction and Pulay scheme of density mixing[10, 11] are applied for the evaluation of energy and stress. All atomic positions in our model have been relaxed according to the total energy and force using BFGS[12] scheme, based on the cell optimization criterion (RMs force of 0.5 eV/nm, stress of 0.1GPa, and displacement of 0.000 2 nm). The calculation of total energy and elec- tronic structure are followed by cell optimization with SCF tolerance of 2.0×10^{-6} eV.



Fig.1 Models of atomic cells used in calculation: (a) Unit cell of MgH₂; (b) Supercell of five times of unit cell of MgH₂

3 Results and discussion

3.1 Equilibrium structure of crystal

The lattice constants of MgH₂ are estimated from the minimized total energy, it can be found that the present lattice parameters a and c of MgH₂ are 0.453 3 and 0.302 2 nm, respectively, which are close to the experimental values[6] of a=0.450 1 nm and c=0.301 0 nm and are also in agreement with the results calculated by SONG et al[5]. The energy of its primitive cell is - 1 010.078 6 eV. The lattice parameters of all the calculation $Mg_8X_2H_{20}$ model are listed in Table 2. It can be found that with the addition of X, the equilibrium lattice constants (*a*) of all the supercell decrease, *c* also decreases, not including Sc and Ti. It can also be found that the unit cell volume of MgH_2 reduces by alloying elements considered (not including Sc) in the present work.

Analysis of the forces shows that the force on the alloying atom is F(X)=0, the forces on Mg2, Mg3, H1 atoms are zero in x and y directions, but nonzero in zdirection, and the forces on H2, H3 atoms are zero in z direction, but nonzero in x and y directions. This indicates that internal relaxation of the atoms within the supercell is carried out for the considered systems. As required by group symmetry, the atoms X and H1 are fixed during the relaxation (Fig.1(b)). And the internal relaxation is performed in two steps. Firstly, Mg2 and Mg3 atoms are relaxed independently along z direction, while H2 and H3 atoms are kept at their initial positions. The variation of the atomic coordinates of Mg2 or Mg3 atoms is defined as $z(Mg2/Mg3)=z - z_0$, where z_0 is the initial atomic coordinate of Mg2 or Mg3 atom (Table 1). The final values of z(Mg2) and z(Mg3) are estimated as listed in Table 2. It can be found that the changes of the positions of Mg2 and Mg3 atoms in the z direction are very small due to the addition of alloying elements, owing to the fact that Mg2 and Mg3 atoms are the second nearest-neighbor atoms, resulting in a small energy difference between the relaxed and un-relaxed positions. Secondly, Mg2 and Mg3 atoms are fixed at their new positions, and H2 and H3 atoms are relaxed along x directions(As required by group symmetry, x=y independently, with the change of x(H2/H3)=x - x_0 , where x_0 is the initial atomic coordinate of H2 or H3 atoms in the supercell (Table 1). The final values of x(H2) and x(H3) are estimated and are

listed in Table 2. It is found that the value of x(H2) is smaller than that of x(H3). This is consistent with the fact that H3 atom is the nearest neighbor of the alloying atom in the present supercell(Fig.1(b)). Therefore, from the structure relaxation study, it is noted that the alloying elements (not including Cu) mainly influence the position of the matrix atoms in their vicinity, i.e. only the positions of the nearest neighbor H3 atoms are significantly changed. The influence of alloying elements on the position of H3 atoms increases in an order of Sc, Zn, Ti, V, Fe, Mn, Co, Ni, Cr.

3.2 Heat of formation

Previous works show that the thermodynamic magnesium hydride aspects of formation/ decomposition are described by pressure-composition isotherms under the given temperature (T). The overall reaction of hydride formation is composed of three steps. Firstly, the host metal dissolves some hydrogen as a solid solution (α phase), keeping alloy structure unchanged. Secondly, when the hydrogen pressure altogether with concentration of H in the host metal is increased, the interactions between hydrogen atoms become locally strong, and the tetragonal structure hydride (β phase) becomes nucleation and growth. While two phases coexist, the isotherms appear a flat plateau, the length of which means that how much H₂ can be stored with small pressure variations, and that the plateau or equilibrium pressure depends strongly on temperature and is related to the changes of enthalpy (ΔH) and of (ΔS) entropy, respectively. Finally, the concentration of H in the host metal show no further change if hydrogen pressure is kept on increasing. The reaction of hydride decomposition is opposite to hydride formation, but exists in time retardation compared with hydride formation. During the second step, it is often related to the equilibrium

Table 2 Equilibrium lattice parameters and total energies of Mg₈X₂H₂₀ supercell model

Element	a/nm	<i>c</i> /nm	<i>z</i> (Mg2)	<i>z</i> (Mg3)	<i>x</i> (H2)	<i>x</i> (H3)
_	0.453 4	1.510 4				
Sc	0.450 5	1.558 4	0.002 595 03	- 0.002 181 60	- 0.001 252 97	0.001 774 56
Ti	0.444 0	1.528 6	- 0.000 271 03	0.000 687 53	- 0.002 506 52	0.005 907 13
V	0.438 9	1.506 2	- 0.002 935 36	0.002 729 59	- 0.003 402 45	0.008 962 64
Cr	0.437 4	1.483 6	- 0.004 179 38	0.002 534 73	- 0.003 750 07	0.011 645 61
Mn	0.437 2	1.459 5	- 0.007 457 80	0.002 658 51	- 0.003 312 61	0.009 316 43
Fe	0.436 8	1.433 8	- 0.010 874 03	0.003 201 53	- 0.002 910 35	0.009 023 58
Co	0.439 8	1.448 0	- 0.010 112 03	0.000 001 40	- 0.001 095 52	0.010 011 10
Ni	0.439 7	1.470 5	- 0.006 616 30	0.002 064 02	- 0.000 759 96	0.010 970 90
Cu	0.441 1	1.494 6	- 0.006 712 03	- 0.001 862 47	0.001 460 48	0.000 026 13
Zn	0.452 2	1.486 9	- 0.002 802 03	0.001 471 53	0.000 546 48	0.004 078 13

hydrogen pressure through Van't Hoff equation[13]:

$$\ln\left(\frac{p}{p_0}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{1}$$

where *P* is flat plateau pressure for decomposition, P_0 is the standard pressure (=0.1 MPa), ΔH is the heat of formation, ΔS is the entropy change, *T* is the temperature and *R* is the gas constant. The entropy change in Eqn.(1) is dominated by the entropy loss of the gaseous hydrogen, roughly 130.8 J/mol[13] for MgH₂ under consideration. Hence, Eqn.(1) can be expressed as

$$\frac{\partial(\ln p)}{\partial(1/T)} = \frac{\Delta H}{R}$$
(2)

From Eqn.(2) it can be found that the heat of formation (ΔH) of magnesium hydride determines the flat plateau pressure of magnesium hydride decomposition under the given temperature(*T*).The smaller the heat of formation (ΔH) is, the lower the pressure is, which indicates the enhanced dehydrogenating properties of magnesium hydride[5, 14]. Hence, one may only concentrate on the heat of formation in order to understand the dehydrogenating properties of magnesium hydride.

Based on the above summary, the heat of formation of MgH_2 can be calculated by[5]

$$\Delta H_{\mathrm{MgH}_{2}} = E_{\mathrm{tot}}(\mathrm{MgH}_{2}) - E_{\mathrm{tot}}(\mathrm{Mg}) - E_{\mathrm{tot}}(\mathrm{H}_{2}) \qquad (3)$$

where $E_{tot}(MgH_2)$ is the energy of primitive cell of MgH₂, $E_{tot}(Mg)$ is the single atomic energy of HCP-Mg in the solid states, and $E_{tot}(H_2)$ is the total energy of hydrogen molecule. The calculation energies of Mg atoms are also listed in Table 1 using the same code as primitive cell model. The total energy of hydrogen molecule is calculated as - 2.320Ry (-31.565 2 eV)[13], using von Barth-Hedin exchange- correlation potential. The present heat of formation of MgH₂ is -62.30 kJ/mol, slightly bigger than the value -73.5 kJ/mol from the thermodynamic data under the given temperature (*T* 673 K) measured experimentally by BOGDANOVIĆ et al[15].

In order to investigate the influence of 3d transition metal alloying elements on the structural stability of magnesium hydride, a parameter (ΔE_r) is used to estimate the relative stability of alloyed magnesium hydrides compared with that of MgH₂. Then, ΔE_r is calculated by[5]

$$\Delta E_{\rm r} = E_{\rm tot} \left(Mg_8 X_2 H_{20} \right) - 10 E_{\rm tot} \left(Mg H_2 \right) - 2[E_{\rm tot} (X) - E_{\rm tot} (Mg)]$$
(4)

where the first two terms on the right-hand side of Eqn.(4) are the total energy of MgH_2 —X with the current supercell and primitive cell of MgH_2 ,

respectively, $E_{tot}(X)$ denotes the total energy of element X and is calculated using the same code as for MgH₂—X. In our calculations, FCC-type structure is used for Mn, Ni, Cu and Zn, respectively, BCC-type structure is used for V, Cr and Fe, respectively, HCP-type structure is used for Sc, Ti, Co and Mg, respectively. The values of $E_{tot}(Mg_8X_2H_{20})$ and $\Delta E_{\rm r}$ calculated here are listed in Table 3. It is found that ΔE_r value in our calculations for MgH₂—Ti system is close to that given by SONG et al[5], but the other values are smaller than those given by SONG et al[5] for $MgH_2 - Fe$, $MgH_2 - Ni$, $MgH_2 - Cu$, respectively. The data in Table 3 also show that the negative heat of formation of magnesium hydride alloyed by X (not including Sc) decreases in comparison with that of MgH₂, and the amount of reduction increases in an order of Fe, Ti, Co, Zn, Ni, V, Mn, Cu and Cr. It is noted that the ΔE_r values for MgH₂—Cu and MgH₂—Cr are very close to the absolute value of the heat of formation of MgH₂, implying the two alloyed systems are more destabilized. Moreover, ΔE_r value for MgH₂—Ni is bigger than that of MgH2-Ti, which is against the experiment result[4]. In fact, some alloying elements(such as Ti, V, Fe, Co, Ni and Cu) considered here can form compounds with Mg and hydrogen, for example, TiH₂, VH_{0.81}, MgCu₂[1, 2], or form complex magnesium hydrides, such as Mg₂FeH₆, Mg₂CoH₅, Mg₂NiH₄ and MgCu₂[3, 4]. The influence of alloying elements considered here on the structural stability of MgH₂ should be addressed by the formation of these second phases, which can be found elsewhere.

3.3 Electronic structure

3.3.1 Density of states

Total and partial density of states (DOS) for MgH₂ are performed as shown in Fig.2. The total DOS shows a few main bonding peaks in the energy range between Fermi level and -7.0 eV. It is found that the main bonding peaks (between Fermi level and -3.0 eV) mainly originates from the contribution of valence electron numbers of H(s), Mg(p) and little Mg(s)orbitals, while the main bonding peaks between -4.0and -3.0 eV are the result of the bonding among H(s), Mg(s) and little Mg(p). The main bonding peaks between -7.0 and -4.0 eV are caused by H(s) and Mg(s). The total DOS in Fig.2 shows that the highest bonding possesses the characteristic of significant s-p hybridization, contributed by the hydrogen s and magnesium p and s electrons. This leads to a relatively high formation energy of MgH₂. This aspect was changed in the alloyed 3d transition metal MgH₂ systems.

The alloying elements considered here can be

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Element		$E_{\rm tot}/{\rm eV}$ —	$\Delta E_{\rm r}$ (kJ/mol)	
	$E_{\rm tot}/(ev \cdot atom)$		Present	Ref.[5]
Mg	- 977.876 7	- 10 100.786	0	
Sc	- 1 279.426 8	- 10 704.261	- 3.436 7	
Ti	- 1 605.250 4	- 11 353.955	15.502 2	22.91
V	- 1 978.863 7	- 12 099.602	30.651 6	
Cr	- 2 468.684 9	- 13 078.190	40.823 9	
Mn	- 653.748 5	- 9 449.360	30.761 9	
Fe	- 865.499 8	- 9 875.240	7.825 4	33.34
Co	- 1 044.284 7	- 10 231.999	15.650 8	
Ni	- 1 356.194 2	- 10 854.850	24.911 3	67.88
Cu	- 1 352.670 4	- 10 846.246	40.007 3	69.12
Zn	- 1 716.249 7	- 11 575.860	16.312 9	

Table 3 Energy of pure metal atom, total energies of Mg₈X₂H₂₀ supercell model and parameter ΔE_r



Fig.2 Total and partial density of states of MgH₂ crystal

classified into three groups: 1) Sc, Ti, V, Cr and Mn; 2) Fe, Co and Ni; 3) Cu and Zn. According to experimental findings^[1-4], in group 1, Ti and V do not form compounds with Mg, but can form hydrides TiH₂ and VH_{0.81}[1, 2], respectively. For group 2, Fe, Co and Ni can form hydrides Mg₂FeH₆, Mg₂CoH₅ and Mg₂NiH₄[3, 4], respectively. For group 3, Cu can form hydrides MgCu₂[2] with Mg. These features are determined by the electronic structure.

1) Sc, Ti, V, Cr, Mn

Fig.3(a) shows the total and partial density of states (DOS) of MgH₂ supercell with alloying system such as Sc, Ti, V, Cr, Mn. In MgH₂-Ti (Fig.3(c)), the bonding peaks near Fermi energy are contributed by Ti(d), the main part, and a weak Mg(s), Mg(p) and H(s) electrons. The s-p bonding peaks between magnesium

and hydrogen appear in the energy range between -2.0and -6.0 eV, there is also weak contribution of Ti(d) electrons to the bonding peaks. The s electron between magnesium and hydrogen appears in the energy region from -6.0 to -9.0 eV. Total and partial density of states (DOS) of MgH₂ - X(X= Sc, V, Cr, Mn) systems are similar to those of MgH_2 - Ti. In MgH_2 - Sc(Fig.3(b)), there is a contribution of the Mg(s), Mg(p), H(s) and a little Sc(d) electrons to the bonding peaks from -2.5 to -7.0 eV, Mg(s) and H(s) electrons bonding appears in the energy region from -7.0 to -9.0 eV. In MgH₂ - V (Fig.3(d)), the bonding peaks between -2.0 eV and -6.0 eV is contributed by Mg(s), Mg(p), H(s) and a little V(d) electrons, while these peaks between -6.0eV and -9.0 eV is the result of the interaction between Mg(s) and H(s) electrons. For MgH_2 - Cr (Fig.3(e)) and MgH_2 —Mn(Fig.3(f)), the bonding peaks (between -1.5 eV and -6.0 eV) are caused by the bonding of Mg(s), Mg(p), H(s) and a little Cr(d) or Mn(d)electrons. The s electron bonding between magnesium and hydrogen all appears in the energy region from -6.0 to -9.0 eV for MgH₂ - X (Sc, Ti, V, Cr, Mn) systems.



Figs.4(a), (b) and (c) show the total and partial density of states (DOS) of MgH_2 —Fe, MgH_2 —Co, MgH_2 —Ni, respectively. In Fig.4(a), it can be found that the bonding peaks of total DOS in the energy range from -0.5 to -1.5 eV show Fe(d) electrons characteristics, while a little Mg(s), Mg(p), H(s) electrons also contribute to some extent. The highest bonding peak in total DOS is located at about -1.0eV below Fermi energy. These feature implies that there is a relatively weak bonding between Fe, Mg and H in the MgH₂—Fe systems. The other bonding peaks in total DOS are located in the energy range from -2.0 to -9.0 eV below Fermi energy. These peaks are the



Fig.3 Total and partial density of states of MgH₂(a), MgH₂—Sc(b), MgH₂—Ti(c), MgH₂—V(d), MgH₂—Cr(e) and MgH₂—Mn(f)

results of the interactions between Mg and H. As far as the highest bonding peak in total DOS at about -4.0eV below the Fermi energy is concerned, it is caused by the bonding of Mg, H1 and H3. In MgH₂— Co(Fig.4(b)), the bonding peaks near Fermi energy are dominated by the strong Co(d), and a weak Mg(s), Mg(p) and H(s) electrons, the highest bonding peak in total DOS is located at about -2.0 eV below Fermi energy, while the second bonding peak at about -5.0 eV below Fermi energy is the results of the interactions of Co, H1 and H3. In MgH₂—Ni (Fig.4(c)), there is a contribution of the main Ni(d) and a weak Mg(s), Mg(p) and H(s) electrons to the bonding peaks near Fermi energy. The highest bonding peak in total DOS is located at about -2.5 eV below Fermi energy. While the bonding peak at about -5.0 eV below the Fermi energy is the results of the interactions between H1(s), H3(s), Mg2(s), Mg3(s), Mg2(p) and Mg3(p), this indicates a relatively stronger interaction between Mg3 and H1 atoms. In partial DOS, the magnitude of the Mg(p) electron peak in the energy range from -2.0 to -4.0 eV is reduced compared with that of MgH₂, which means a relatively weak interaction between Mg and H atoms.

3) Cu, Zn

Fig.5 shows the total and partial density of states (DOS) of MgH₂—Cu and MgH₂—Zn. In Fig.5(a), the main bonding peaks near Fermi energy are contributed by Cu(d), Mg(p) and H(s) electrons. The contribution of H2(s) electron to the peak is smaller than that of the other two H atoms. The highest bonding peak, located at -3.0 eV, shows the characteristics of Cu(d) electrons, but it also contains the contributions of Mg2(p) and H2(s) electrons. The other peaks are caused by the bonding of Mg2(p), Mg3(p), H1(s), H3(s), with some level of the Cu(d) electrons. In MgH₂—Zn (Fig.5(b)), the main bonding peaks near Fermi energy are dominated by Zn(d), Mg(p) and H(s) electrons, while the highest bonding peak, located at -6.0 eV, is the result of the bonding between main Zn(d) and weak Mg(s) and H(s) electrons. The other peaks are dominated by Mg2(p), Mg3(p), H1(s) and H3(s)

electrons.

3.3.2 Bonding and charge density distribution

In order to understand the intrinsic mechanism of the bonding and influence of 3d transition metal alloying on the structural stability of MgH₂, a charge density analysis was carried out on (1 1 0) plane. Fig.6 shows the charge distribution on (1 1 0) plane of MgH_2 and the considered alloying systems. Fig.6(c) shows the charge distribution of MgH₂—Ti systems. Ti-H1 and Ti-H3 bonds can be identified, while Mg3—H2, and Mg2—H3, Mg2—H2, and Mg3—H3 bonds are similar to the case of MgH₂, but Mg2-H2, and Mg3-H3 bonds slightly reduces. The bonds of MgH_2 —Sc, MgH_2 —V, MgH_2 —Cr, MgH_2 —Mn systems are similar to that of MgH₂-Ti, which can be seen in Figs.6(b), 6(d), 6(e), 6(f), respectively. For MgH_2 —Fe(Fig.6(g)), MgH_2 —Co(Fig.6(h)) and MgH_2 -Ni (Fig.6(i)), the bond strength between Mg and H atoms is reduced by addition of Fe, Co, or Ni. The charge distribution on (110) plane of MgH₂-Cu, $MgH_2 - Zn$ systems is shown as Fig.6(j), 6(k), respectively. It is found that the distributions of electrons between Mg and H atoms are similar to that in the MgH₂ systems by addition of Cu or Zn. Only the Mg2-H2 bond are slightly weakened.

3.4 Dehydriding properties

The influence of alloying elements on the



Fig.4 Total and partial density of states of MgH₂—Fe(a), MgH₂—Co(b) and MgH₂—Ni(c)



Fig.5 Total and partial density of states of MgH₂—Cu(a) and MgH₂—Zn(b)

dehydrogenation properties of MgH₂ was investigated experimentally, such as Ni, Co, Mn, Cu, Ti, Fe and V. It is found that the dehydrogenation properties are improved by the addition of above these alloying elements. For MgH₂-Ti system, due to the formation of the second phase $TiH_2[2]$, the hydrogen atoms is held by Ti atoms. However, DOS (Fig.3(c)) and the charge distribution on (110) plane (Fig.6(c)) of the system show that the bonding strength between Mg and H atoms is slightly reduced, compared with that of MgH₂, and the unit cell volume is also reduced in this system(Table 2).Hence, the structural stability of MgH₂ is reduced, then the dehydrogenation properties of MgH₂ is improved by addition of titanium. The alloving element V, Mn, shows a similar effect to Ti due to their similar electronic structure features shown Figs.4(d),.4(e) and 8(d), 8(e), respectively. But for MgH_2 —Cr systems, the positions of the nearest neighbor H3 atoms with alloy atoms are significantly changed(Table.2), which indicates the strongest bond between Cr and H3 exist and this lead to the weaker bond between Mg and H. Hence, the dehydrogenation properties of MgH₂ is significantly improved by addition of Cr. For MgH₂ - Sc systems, the dehydrogenation properties of MgH₂ is not be improved, it could be caused by unit cell volume increased[13], which should be further studied. For

MgH₂—Fe and MgH₂—Co systems, the stability of the considered system is reduced by 7.825 4 kJ/mol and 15.650 8 kJ/mol(Table 3), respectively. Weak bonding peak near the Fermi energy were found in DOS (Figs. 4(a) and 4(b)) and the charge distributions on (110) plane(Figs.6(g) and 6(h)) also show a reduction of the electron density between Mg and H atoms. Therefore, the dehydrogenation kinetics of MgH₂ is improved by addition of Fe or Co. For MgH₂—Ni systems, the dehydrogenation kinetics of MgH₂ is significantly improved compared with that of MgH₂—Fe and MgH₂—Co by addition of Ni as mentioned above(see Table 3). The structural stability of the considered system is reduced by 24.911 3 kJ/mol, which can be expected due to the fact that means that the formation of the second phase Mg₂NiH₄ with a heat of formation of - 62.7 kJ/mol $H_2[16]$, larger than that of MgH₂. This indicates that the H atoms in the mixture of MgH₂ and Mg₂NiH₄ compounds can be released more readily than those in MgH₂. Hence, The structural stability of MgH₂—Ni systems is lower than that of MgH₂—Fe and MgH₂— Co systems. For MgH₂—Cu systems, the parameter (ΔE_r) is close to the absolute value of the heat formation of MgH₂. It is found that the weaker bonds between Mg and H_2 is seen as Figs.5(a) and 6(j). And due to the formation of MgCu₂, Mg atoms are



Fig.6 Charge distribution on (110) plane of MgH_2 (a), MgH_2 —Sc(b), MgH_2 —Ti(c), MgH_2 —V(d), MgH_2 —Cr(e), MgH_2 —Mn(f), MgH_2 —Fe(g), MgH_2 —Co(h), MgH_2 —Ni(i), MgH_2 —Cu(j) and MgH_2 —Zn(k)

completely held by Cu atoms. Hence, the previously engaged H atoms can be readily released from MgH₂ —Cu systems, leading to the improvement of the dehydrogenation properties of MgH₂. the alloying elements Zn shows a similar effect to Cu by the analysis the electronic structure shown in Figs.5(b) and 6(k), but Mg atoms are not completely held by Zn atoms, which can be seen in Fig.5(b).

4 Conclusions

1) From the relaxation study, it is noted that the alloying elements (not including Cu) mainly influence the position of the matrix atoms in their vicinity: i.e., only the positions of the nearest neighbor H3 atoms are significantly changed. The influence of alloying elements on the position of H3 atoms increases in an order of Sc, Zn, Ti, V, Fe, Mn, Co, Ni and Cr.

2) Through calculations of the negative heat formation of magnesium hydride alloyed by X (X denotes 3d transition metal) element, it is found that when a little X (not including Sc) dissolve into magnesium hydride, the structural stability of alloying systems decreases, which indicates that the dehydrogenation properties for MgH_2 is improved.

3) After comparing the densities of states (DOS) and the charge distribution of MgH_2 with and without X alloying, it is found that the improvement for the dehydrogenation properties of MgH_2 alloyed by X attributes to the fact that the weakened bonding between magnesium and hydrogen is caused by the stronger interactions between X (not including Cu) and hydrogen.

4) For MgH₂—Cu systems, the parameter ΔE_r is close to the absolute value of the heat formation of MgH₂. This may mainly be due to the formation of MgCu₂, in which Mg atoms are completely held by Cu atoms, and the previously engaged H atoms can be readily released from MgH₂—Cu systems. But for MgH₂—Cr systems, the positions of the nearest neighbor H3 atoms with alloy atoms are significantly changed, which means that the strongest bond between Cr and H3 exist and this lead to the weaker bond between Mg and H. Therefore, the dehydrogenation properties for MgH₂ is significantly improved by addition of Cu or Cr.

5) The calculation results of the improvement for the dehydrogenation properties for MgH_2 —X (X=Ti, V, Mn, Fe, Co, Ni, Cu) systems are in agreement with the experimental results. The dehydrogenation properties for MgH_2 are expected to be improved by addition of Cr, Zn alloying elements.

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