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Full Length Article

First-principles calculation of hydrogen adsorption and diffusion on Mn-doped Mg_2Ni (010) surfaces

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ABSTRACT

Effects of Mn doping on the hydrogen adsorption and diffusion on the Mg_2Ni (010) surface are studied using first-principles density functional theory. The results show that the Mg_2Ni (010) surface becomes more uneven and the thermodynamical stability of Mg_2Ni (010) system is lowered after Mn doping. Analysis of the hydrogen adsorption energies on the pure and Mn-doped Mg_2Ni (010) surfaces shows that Mn-doped Mg_2Ni (010) surface has more sites for hydrogen to adsorb stably. Further calculation of the hydrogen diffusion indicates that the substitution of Mg with Mn lowers the energy barrier for hydrogen to diffuse from the (010) surface to the subsurface.

1. Introduction

Hydrogen has received an increasing focus as one of the most promising substitutes for fossil fuels with many advantages as a sustainable and renewable energy [1,2]. It is an abundant energy supply and can lead to zero emission. However, developing a safe and efficient hydrogen storage system at room temperature and atmospheric pressure is a major challenge [3,4].

Recently, the Mg_2Ni alloy was extensively investigated as a potential hydrogen storage material because of its high capacity, good safety, low cost, relatively mature preparation technology and good reversibility [5–7]. However, the poor hydriding/dehydriding kinetics and the high thermodynamical stability of its saturated hydride makes this alloy far from practical application [8,9]. The design of Mg_2Ni alloy with improved hydriding/dehydriding kinetics through minute substitution of a transition metal was pursued [10–12]. Among these metals, Mn was experimentally predicted to be an idea dopant for Mg_2Ni alloy [13–15]. Further theoretical work showed that the $Mg_{(6i)}$ lattice site is the most preferable site for Mn to occupy in Mg_2Ni lattice [16]. Our recent investigations predicted that the charge/discharge cycles are elevated until the Mn doping content is enough high to form Mg_3MnNi_2 intermetallic compound [17]. Furthermore, the binary compound Mg_2Ni may transform into a cubic phase of Mg_2NiH_4 after absorbing enough hydrogen. This promoted the studies of the effect of transition metal doping on thermodynamical stability and the hydrogen kinetic properties of Mg_2NiH_4 [18,19]. However, the experimental results showed that $Mg_2NiH_{0.24}$ are the main precursors of Mg_2NiH_4 when the binary compound Mg_2Ni alloy adsorbed a small amount of hydrogen atoms [20]. These precursors keep a structure of Mg_2Ni. The mechanisms of surface hydrogen adsorption and bulk hydrogen diffusion are difficult to be determined only from experiments [21]. Therefore, the behaviours of hydrogen adsorption and diffusion on the pure and Mn-doped Mg_2Ni (010) surfaces should be carried out to clarify the essence of the enhanced hydriding kinetics of the Mn-doped Mg_2Ni alloy. This study not only contributes to a deeper understanding of the mechanisms of hydrogen adsorption on the Mg_2Ni surface, but also helps to explore novel hydrogen storage materials with improved hydrogen storage properties. However, rare reports have shed light on this issue to date.

Here, the effects of Mn doping on the mechanisms of hydrogen adsorption and diffusion on the Mg_2Ni (010) surfaces were investigated using first-principles density functional theory (DFT) calculations. The influence of substituting Mn on structure, electronic properties and thermodynamic stability of (010) Mg_2Ni surfaces were discussed in detail. The diffusion energy barriers for a single hydrogen atom from the pure and Mn-doped Mg_2Ni (010) surfaces to the subsurface were calculated.

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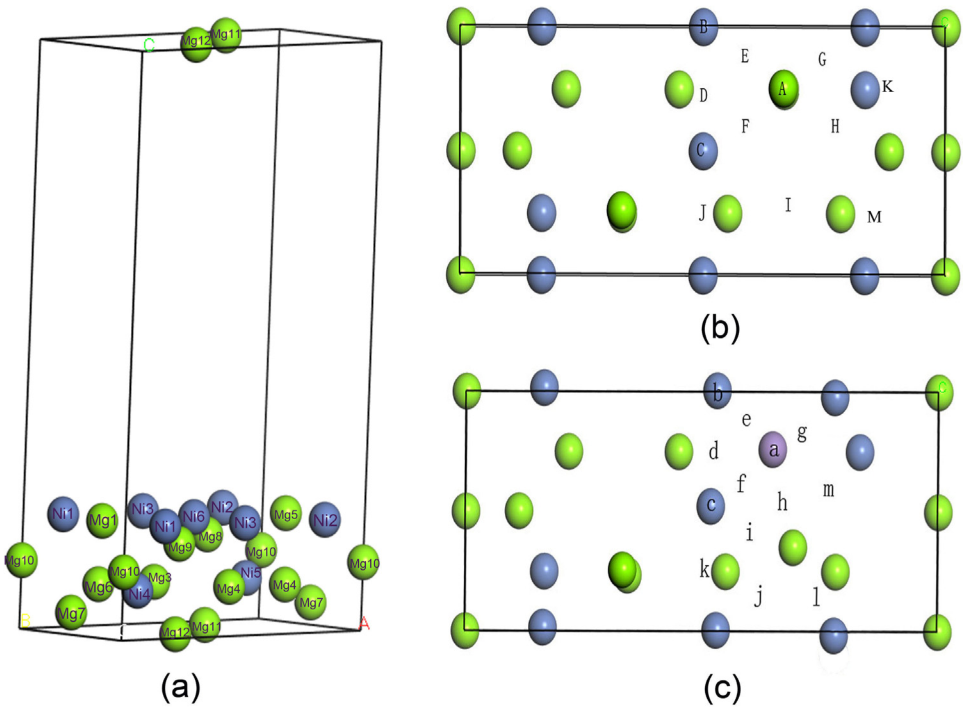

Fig. 1. Structure of Mg_2Ni (010) surface: (a) side view of the pure surface, (b) top views of the pure surface, (c) the Mn-doped surface.

2. Calculation models and method

Mg_2Ni alloy has a hexagonal structure, belonging to the P6222 space group (No. 180) with lattice parameters $a = 5.219$ Å and $c = 13.293$ Å [22]. Each unit cell contains six formula units, expressed as Mg_2Ni. The 12 Mg atoms occupy the 6f and 6i lattice sites, while the six Ni atoms occupy the 3b and 3d lattice sites. All calculations were performed using the Cambridge Serial Total Energy Package (CASTEP), which is a first-principles plane wave pseudopotential method based on DFT [23]. Ultrasoft pseudopotentials [24] in reciprocal space were used. The Perdew Burke Ernzerhof (PBE) functional in the generalized gradient approximation (GGA) [25] was adopted as the exchange-correction functional. The crystal reciprocal-lattices were integrated over the symmetrized Brillouin zone by summing over the special k-points generated using the Monkhorst-Pack scheme [26]. 9 × 9 × 9 and 13 × 1 × 13 k-point meshes were employed for Mg_2Ni bulk and (010) surface, respectively. A plane-wave basis cutoff energy of 340 eV was used to ensure the calculations converged for the total energies and forces acting on the atoms. A finite basis set correction and the Pulay density mixing scheme [27,28] were applied to evaluate the energy and stress. In all the cases, self-consistency iterations were achieved with a tolerance in total energy of 10^{-6} eV and the residual force of each atom was less than 0.01 eV/Å. Convergence of the calculations was carefully checked with respect to the plane-wave cutoff and the number of k points used in the summation over the Brillouin zone. The linear synchronous transit (LST) method was implemented to inspect the diffusion energy barrier for hydrogen atom on the pure and Mn-doped Mg_2Ni (010) surfaces. After geometry optimization, the lattice parameters of the bulk Mg_2Ni were a = b = 5.217 Å, c = 13.274 Å, which agrees well with the experimental values (a = b = 5.219 Å, c = 13.293) Å [29] and previous theoretical results [14,22]. The Mg_2Ni (010) surface was modeled as periodically slabs with six layers. The slab was separated from its periodic image in the direction normal to the surface by a vacuum space of 16 Å. Slab calculations allowed three surface layers to relax, holding the remaining layers fixed in their optimized bulk positions [30,31].

3. Results and discussions

3.1. Pure and Mn-doped Mg_2Ni (010) surfaces

Fig. 1(a) shows the side view of a pure Mg_2Ni (010) surface. There were eight atomic sites on the top layer of the pure Mg_2Ni lattice (010) surface. These were named Ni_1, Ni_2, Ni_3, Ni_6, Mg_1, Mg_5, Mg_8 and Mg_9, respectively. Fig. 1 (b-c) shows the top views of the pure and Mn-doped Mg_2Ni (010) surfaces. The majuscule and the minuscule signs represented the possible sites for hydrogen to adsorb in the doped region. Before replacement with Mn, the $Mg_{(1,5)}$ and $Mg_{(8,9)}$ were labeled as $Mg_{(6f)}$ and $Mg_{(6i)}$, respectively, and Ni_6 was labeled as $Ni_{(3d)}$ and $Ni_{(1,3,2)}$ was $Ni_{(3b)}$ according to the atomic position in the Mg_2Ni lattice.

Generally, the structural stability of the crystal is closely correlated to its formation enthalpy $\triangle E_{form}$. The negative formation enthalpy implies an exothermic process. Lower enthalpy of formation values implies a more stable crystal [32]. Therefore, calculations regarding the effect of Mn doping sites on the formation energy of the Mg_2Ni (010) surface were performed to identify that sites that the dopant Mn prefers. The formation energy of dopants is defined as [33]:

$$\varDelta E_{form} = E_{doped-slab} - E_{slab} - E_{Mn} + E_{Ni/Mg} \qquad (1)$$

Here, $E_{doped\text{-}slab}$ and E_{slab} are the total energy of the Mn-doped and pure Mg_2Ni (0 1 0) surface, respectively. The E_{Mn} and $E_{Ni/Mg}$ are the total energy of Mn and Ni/Mg atoms, respectively. The formation energies of the relaxed surfaces with the $Mg_{(6f)}$ and $Mg_{(6i)}$ atoms substituted by Mn atom were 0.135 and 0.098 eV, respectively, and these energies of the relaxed systems with the $Ni_{(3b)}$ and $Ni_{(3d)}$ atoms replaced were 1.650 and 1.374 eV, respectively. From the above mentioned data, one can find that although the $Mg_{(6i)}$ atoms are more easily replaced by the Mn atom due to the lower formation energy, the formation energy values of Mn-doped Mg_2Ni (010) surfaces were positive suggesting that the doping processes decrease the stability of the Mg_2Ni (010) surface. This is consistent with the experimental and theoretical results reported in the literature