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Stability and hydrogen adsorption properties of Mg/Mg₂Ni interface: A first principles study

Yuying Chen, Jianhong Dai, Yan Song*

School of Materials Science and Engineering, Harbin Institute of Technology at Weihai, 2 West Wenhua Road, Weihai, 264209, China

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ABSTRACT

The stability and hydrogen adsorption behaviors of Mg/Mg₂Ni interface were studied by first principles calculations. Results demonstrated that the interaction between Ni (from Mg₂Ni compound) and Mg (from Mg metal) is the key factor stabilizing the interface, and the interface provides a medium to capture hydrogen atoms originating from the accumulation of electrons in the interface zone by the formation of the interface. Hydrogen atoms adsorbed in the interface zone tend to form covalent bonds with metal atoms (Ni and Mg atoms), which deliver negative adsorption energies in the range of -0.831 to -0.019 eV for most possible adsorption sites. However, the strength of the H-metal bonds depends on the environment the H located. The present study illustrates that the Mg/Mg₂Ni layered structure could be a potential medium for reversible de/hydrogenation processes.

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Introduction

Hydrogen as an elemental energy substance has drawn much attention due to its efficient, clean, and recyclable, which make it be an ideal energy medium that is alternative to fossil fuels. However, the storage and transportation of hydrogen affects its efficient use. Mg-based hydrogen storage materials are one of the most promising hydrogen storage media due to its high hydrogen content and low cost, but suffered from large formation enthalpy (-75 kJ/molH₂ for MgH₂) and poor hydrogen ab/desorption performance that hinder its practical application [1].

Many efforts have been made to improve the thermodynamics and the kinetics of MgH₂ in the past decades. It is possible to dramatically modify the thermodynamic properties of a thin metallic film by means of slightly changing the

architecture of the binary magnesium hydride samples [2]. An increase of surface area, formation of micro/nanostructures, and creation of defects on the surface or in the interior of the materials can effectively improve the H₂ adsorption and desorption properties of MgH₂ [3]. And the combination of doping and strain is a more efficacious method to improve the H₂ desorption performance from MgH₂ surfaces [4,5]. First principles molecular dynamics calculations also illustrated that nanoclusters are helpful to increase the hydrogen diffusion rate and lower the desorption temperature of MgH₂ [6].

In recent years, multilayer materials have attracted extensive attention regarding to hydrogen storage. A coating strategy not only effectively improves hydrogen ab/desorption properties but also provides an alternative route for the preparation of transition metal complex hydrides [2,7–18]. Baldi et al. reported that the thermodynamic stability of the Mg–H film system can be drastically modified due to the

* Corresponding author.

E-mail address: sy@hitwh.edu.cn (Y. Song).<https://doi.org/10.1016/j.ijhydene.2018.07.031>

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existence of elastic constraints [7]. Chung et al. investigated hydrogenation performance of the Mg–Pd thin films and pointed out that the formation enthalpy of hydride is altered when the strong Pd–Mg bonds were broken [8]. Theoretical works suggested that the charge accumulation at the interface plays a positive role in capturing hydrogen atoms [9,10]. Liu et al. found that alloying some elements such as Si, Ti, Fe, Co, and Ni in Mg not only promote the hydrogen uptake but also improve the desorption dynamics and kinetics, and Ni is the most effective catalyzed element among them. Coating Mg with Ni could significantly accelerate hydrogen ad/desorption process, whose thermodynamics and kinetics properties about hydrogenation reaction are better than the bare Mg nanoparticles [8,13–15]. Previously, we have studied the hydrogen adsorption characteristics of Mg/Ni interface [9]. The results reveal that the Mg/Ni interface provides a promising space for hydrogen atoms to be adsorbed with relatively low adsorption energy. The adsorption of hydrogen atoms will strengthen the connection between Mg and Ni layers. Experimental investigation by Tsai et al. indicated that the Mg/Ni interface could generate the Mg/Mg₂Ni interface due to the diffusion of Mg [19]. It is also known that the binding energy of Mg 2p electrons varies from 49.5 eV in Mg, 53.8 eV in MgH₂, 49.2 eV in Mg₂Ni, to 50.1 eV in Mg₂NiH₄, and the binding energy of Mg 2s electrons changes in the same pattern as well [20]. Thus there is high possibility to form a Mg/Mg₂Ni interface in a Mg–Ni layered structure. Therefore, we investigate formability and stability of the Mg/Mg₂Ni interface and its hydrogen adsorption properties by performing first principles total energy calculations and electronic structure analysis in this work.

Computation method

All calculations were performed using Vienna ab initio simulation package (VASP) based on density functional theory (DFT) [21]. The projector augmented wave (PAW) approach is used to describe the interaction between ionic core and valence electrons, and the generalized gradient approximation (GGA) of Perdew–Wang 91 (GGA-PW91) was adopted to elaborate exchange–correlation function [22,23]. Recently, the hybrid functionals (HSE) have been used to improve the calculation precision, especially regarding to the band gap. It is reported that the energies required to add (subtract) a H atom in MgH₂ are 2.01 (1.51) eV with GGA and 2.01 (1.52) eV with HSE, respectively [24]. The difference of the hydrogen adsorption energies in MgH₂ calculated with PW91, PBE, PBE0, and HSE06 is less than 0.5% [25]. Those results show that the exchange–correlation functionals have weak influence on the energies for the Mg hydrides. In the present work, the main focus is on the stability and hydrogen adsorption properties, thus all calculations are performed at the GGA level. And we did not use the time-consuming HSE functionals by considering the computational resources.

The convergence of total energy on the cutoff energy was examined for the interface (Inters1) by varying the cutoff energy from 300 eV to 600 eV with an interval of 50 eV. The convergence of total energy is in the range of 0.001 eV when the cutoff energy is beyond 500 eV. Meanwhile the variation of

total energy for k-meshes of $4 \times 4 \times 1$, $5 \times 5 \times 1$, $6 \times 6 \times 1$ and $7 \times 7 \times 1$ is within 0.009% relative to the absolute value of total energy [26]. Therefore a plane-wave basis set with a cutoff energy of 500 eV and a $4 \times 4 \times 1$ Monkhorst–Pack k-points mesh were used for all calculations based on the considerations of accuracy and consumption of computer resources. The convergence criteria for self-consistency calculations are that the differences between two consecutive energies and forces on each atom are less than 0.01 meV and 0.01 eV/Å, respectively.

Results and discussions

Mg₂Ni has a hexagonal structure with space group P₆222 (No 180) and the lattice parameters are $a = b = 5.219$ Å, $c = 13.293$ Å [27]. Further, the lattice parameters of hcp Mg are $a = b = 3.21$ Å, $c = 5.21$ Å [28]. In order to check the accuracy of the calculations, we first optimized the crystal structures of Mg₂Ni and Mg. The resulted lattice parameters are $a = b = 5.185$ Å, $c = 13.294$ Å for Mg₂Ni, and $a = b = 3.209$ Å, $c = 5.211$ for Mg, respectively, which are in good agreement with the experimental data. Based on the experimental findings that Mg₂Ni and Mg crystallites in deposited film were preferentially grew with their (001) crystalline plane [29], a 3×3 Mg (0001) and 2×2 Mg₂Ni (001) surface supercells were employed to stack the Mg/Mg₂Ni interface model along the c direction. The size of the supercell was that the on plane axis $a = b = 10.02$ Å to ensure a small lattice misfit between the Mg (0001) plane and Mg₂Ni (001) plane, and c is in the range from 39.4 Å to 40.4 Å with a vacuum thickness of 15 Å. The supercell contains five atomic layers in the Mg side meanwhile 12 atomic layers in the Mg₂Ni side, and 93 Mg and 24 Ni atoms in total. In the Mg₂Ni slab the atomic layers are repeated every 4 layers, and thus four possible stacking models between Mg and Mg₂Ni slabs were built to model the Mg/Mg₂Ni interface as illustrated in Fig. 1.

Stability of interface

The work of adhesion (W_{ads}) was estimated to identify the stability of the interface via following definition:

$$W_{\text{ads}} = \frac{1}{A} \left(E_{\text{tot}}^{\text{inter}} - E_{\text{Mg}}^{\text{slab}} - E_{\text{Mg}_2\text{Ni}}^{\text{slab}} - \frac{x}{2} E_{\text{H}_2} \right) \quad (1)$$

where $E_{\text{tot}}^{\text{inter}}$ represents the total energy of Mg (0001)/Mg₂Ni (001) interface with ($x = 1$) or without H ($x = 0$). $E_{\text{Mg}}^{\text{slab}}$ and $E_{\text{Mg}_2\text{Ni}}^{\text{slab}}$ are the total energies of individual Mg (0001) and Mg₂Ni (001) slabs, and A is the area of the interface. Fig. 1(c) illustrates the work of adhesion versus with the separation between Mg (0001) and Mg₂Ni (001) slabs. The curve is calculated by rigidly varying the separation of Mg/Mg₂Ni slabs from 1.4 to 2.8 Å in an interval of 0.2 Å without relaxing atomic coordinates and fitted using the Universal Binding Energy Relation (UBER) as below [30].

$$\frac{W_{\text{ads}}}{W_0} = \left(1 + \frac{d - d_0}{l} \right) \exp \left[\frac{d - d_0}{l} \right] \quad (2)$$

where d is the separation between the Mg and Mg₂Ni slabs, d_0 is its equilibrium value, and l is a Thomas–Fermi screening

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