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Hydrogen adsorption and dissociation on nickel-adsorbed and -substituted $Mg_{17}Al_{12}$ (100) surface: A density functional theory study

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ABSTRACT

Adsorption and dissociation properties of hydrogen on Ni-adsorbed and -substituted $Mg_{17}Al_{12}$ (100) surface are investigated systematically by means of the density functional theory calculations. Results show that one Ni atom prefers to adsorb on Mg–Mg bridge site of the surface with adsorption energy -4.90 eV. For substitution systems, the $Mg_{17}Al_{12}$ (100) surface doped with 3.94 wt% and 7.69 wt% of Ni are considered. It is obtained that Ni atoms tend to replace Mg atoms occupied at the subsurfaces. With the addition of Ni, the energy of atomic (molecular) hydrogen adsorption (dissociation) on the $Mg_{17}Al_{12}$ (100) surface are significantly improved. The dissociation of H_2 on the Ni-adsorbed surface is spontaneous. The mechanisms analyses based on the density functional theory are in line with the experimental results.

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Introduction

Magnesium-aluminum (Mg–Al) alloys as typical hydrogen storage materials can be used for hydrogen fuel cells. The reversible reaction for Mg–Al alloy hydrogenation and dehydrogenation can be described as follows [1]:



A great number of studies have been explored to understand the hydrogen storage mechanism of Mg-based hydrides,

and various attempts have been made to promote the hydrogen adsorbing/desorbing characteristics. Experimentally, the thermodynamical and kinetic properties of MgH_2 for hydrogen storage are improved via ball-milling and/or adding small amounts of other metal elements or catalysts [2–6]. Theoretically, the hydrogen storage properties of MgH_2 doped with alkaline metal (Ca, Sr, and Ba) [7] or transition metal (Ti, V, Mn, Fe, Co, Ni, Cu, Zr and Nb) were studied by using density functional theory (DFT) and kinetic Monte-Carlo simulations, etc [8–22]. Calculations show that metal dopants do provide a catalytic effect on H desorption. Among above studies, Lakhal

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et al. [23] studied that Ni presents the highest performances and the best kinetic properties compared to other transition metals (Al, Ti, V, and Fe).

For $Mg_{17}Al_{12}$ alloy, as a principal reactant in the reaction (1), a few investigations have been found. Recently, the effect of Ni addition on hydrogen storage properties of $Mg_{17}Al_{12}$ has been studied by Lee et al. [24]. They found that Ni acts as an efficient catalyst. Compared with ball-milled $Mg_{17}Al_{12}$ alloy, the hydrogen capacities and adsorption rates of $Mg_{17}Al_{12}-X$ wt% Ni ($X = 0, 10, 20$) alloys are enhanced below 300 °C. Most recently, Guo et al. [25] have investigated the mechanism of different transition metals (TM = Ti, V, Ni) doping in Mg–Al alloys ($Mg_{85}Al_{15}+5$ wt%TM). They reported that the hydrogenation/dehydrogenation temperatures and the hydrogenation kinetics of the Mg–Al alloys are optimized after the addition of Ti, V, and Ni. Partially the onset temperature of hydrogenation for the Mg–Al alloy is decreased from 188 °C to 96 °C and the reversible hydrogen storage capacity is increased from 4.21 wt% to 5.58 wt% with the addition of Ni, at 360 °C.

In fact, the surface effect of Mg–Al alloys reaction with hydrogen is very important for understanding the mechanism of hydrogen storage. In our latest work, the hydrogen adsorption, dissociation, and incorporation on (in) $Mg_{17}Al_{12}$ (100) surface have been studied by using the DFT method. The adsorption energies, dissociation barriers, various diffusion pathways, penetrative procedures, and electronic structures of hydrogen on $Mg_{17}Al_{12}$ (100) surface are discussed [26]. In this work, the adsorption and dissociation behaviors of hydrogen on Ni-containing $Mg_{17}Al_{12}$ (100) surfaces, including the nickel-adsorbed and -doped surfaces, have been investigated. The research aim is to explain the catalytic effects of Ni on hydrogenation properties of Mg–Al alloys.

Calculation method

All the calculations were performed using the Vienna ab initio simulation package (VASP) [27,28] based on the density functional theory (DFT) with the projector-augmented wave method (PAW) [29,30]. The exchange correlation energies were evaluated with the Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA) [31]. A $6 \times 6 \times 1$ Monkhorst–Pack k-point mesh [32] was used to sample the whole Brillouin's zone in different (100) surfaces. Atomic and molecular hydrogen as well as Ni atoms were adsorbed on the one side of the target slabs. Periodically repeated slabs were separated by a 15 Å vacuum to avoid the interference between neighboring slabs. In all systems, the atomic position of the adsorbates and the outmost four layers containing 16 atoms were relaxed (seen in Fig. 1), and the rest of the $Mg_{17}Al_{12}$ (100) layers with 42 atoms were frozen in their bulk positions. To obtain the correct interfacial properties, the vdW density functional (vdW-DF) was considered [33]. Testing calculations show that the adsorption energies of hydrogen on the Ni-containing surfaces without vdW functional have higher values than that of vdW ones. For instance, the adsorption energies of H on $Mg_{16}NiAl_{12}$ (100) surface are -0.29 eV (without vdW) and -0.31 eV (with vdW), respectively. Furthermore, the spin-polarized calculation was performed for the Ni-

containing systems. The cutoff energy for the plane wave basis set was fixed at 330 eV. The convergence criteria for total energy and the Hellmann-Feynman force were taken as 10^{-5} eV and 10^{-2} eV/Å, respectively.

For searching the reaction pathways of hydrogen molecules dissociation on different surfaces, the nudged elastic band (NEB) methods were performed to obtain the transition states and barriers energies.

The adsorption energies E_{ads} were calculated as:

$$E_{ads} = \frac{1}{N} (E_{surface/adsorbate} - E_{surface} - N \times E_{adsorbate}),$$

where N is the number of adsorbates, $E_{surface/adsorbate}$ is the total energies of total systems, $E_{surface}$ stands for the total energy of $Mg_{17}Al_{12}(100)$ surface, $Mg_{17}Al_{12}(100)/Ni$ surface, and $Mg_{17-x}Ni_xAl_{12}$ (100), $x = 1, 2$ surfaces, respectively. $E_{adsorbate}$ is the total energies of Ni, $\frac{1}{2}H_2$, and H_2 , respectively.

Results and discussion

Nickel-adsorbed and -substituted on $Mg_{17}Al_{12}$ (100) surface

Firstly, the adsorption and substitution of Ni atoms on $Mg_{17}Al_{12}$ (100) surface are investigated. In Fig. 1, the crystal structures of clean $Mg_{17}Al_{12}$ (100) surface and the possible sites for Ni adsorption and substitution are displayed. The bulk $Mg_{17}Al_{12}$ is crystallized in the body-centered cubic structure (I43 m, space group No.217) at ambient conditions [34]. In details, the atomic positions of Mg are the 2a (0, 0, 0), the 8c (0.32440, 0.32440, 0.32440), and the 24 g (0.35622, 0.35622, 0.03925), marking by Mg1, Mg2, and Mg3, respectively, and the position of Al atom is the 24 g (0.08996, 0.08996, 0.27681).

In this work, the calculated equilibrium lattice parameter for the bulk $Mg_{17}Al_{12}$ alloy is 10.54 Å being in good agreement with the experimental value (10.55 Å) [34]. For the Ni-adsorbed surfaces, the crystal structures of Ni-adsorbed $Mg_{17}Al_{12}$ (100) surface ($Mg_{17}Al_{12}$ (100)/Ni) consists of 34 Mg atoms, 24 Al atoms and 1 Ni atom in a unit cell. For the Ni-doped surfaces, the $Mg_{17-x}Ni_xAl_{12}$ (100) surface has 34-x Mg atoms, 24 Al atoms and x Ni atoms, where the $x = 1$ or 2 corresponding to Ni doped concentration of 3.94 wt% or 7.69 wt%.

According to the model of the $Mg_{17}Al_{12}$ (100) surface plotted in Fig. 1, six adsorption sites of adsorbates, including top site of the Mg1 atom (A), top site of the Mg3 atom (B), bridge site of the Mg3–Mg3 (C), bridge site of the Mg1–Mg1 (D), short bridge site of the Mg1–Mg3 (E), and long bridge site of the Mg1–Mg3 (F), are examined. Results show that the six adsorption sites are good candidates for Ni adsorption. The calculated adsorption energies of Ni on the A–F sites are -1.86 eV (A), -1.92 eV (B), -4.89 eV (C), -4.33 eV (D), -4.43 eV (E), and -4.63 eV (F), respectively. It gains that the Ni atom on the C site is the most stable structure. The preferred site of Ni adsorption on $Mg_{17}Al_{12}$ (100) surface is consistent with that of hydrogen on $Mg_{17}Al_{12}$ (100) surface [26]. Fig. 2 displays the optimized structures and the charge density differences of the Ni-containing $Mg_{17}Al_{12}$ (100) surfaces. As plotted in Fig. 2(a), it is observed that after optimization, the Ni embeds into the

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