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Role of metal impurity in hydrogen diffusion from surface into bulk magnesium: A theoretical study

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ABSTRACT

We have systematically studied the role of four typical metal impurities (Ti, Nb, Al, and In) in the diffusion of hydrogen atoms into magnesium bulk by first-principles calculations. We find that Ti, Nb, and Al energetically prefer to substitute Mg atoms in the inner layers rather than the outmost layer, which In favors, with the consideration of H adsorption. The existence of the subsurface Ti or Nb atoms enhances hydrogen atom diffusion with respect to the pure Mg system, beneficial to the formation of H–Mg–H trilayer structure and its subsequent transition to Mg hydride. The doped Al or In atoms, however, provide no obvious help to the formation of MgH₂.

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1. Introduction

The widely challenged energy crisis and environmental pollution are intensively associated with the large amounts carbon dioxide produced by limited fossil fuels [1], which could be replaced by many environment friendly energy sources, such as solar, wind, biomass energies etc. For the ultimate utilization of these renewable energies, especially in mobile industry, hydrogen energy is vital due to its high energy density and clean product, as well as easily transformed to various energy forms [2]. One of the key issues for the applications of hydrogen fuel cell technology is to find safe and efficient hydrogen storage materials. Hydrogen storage materials mainly include conventional metal hydride, chemical hydrides, complex hydrides, and sorbent systems [3], but the challenge remains for finding suitable hydrogen storage materials to satisfy U.S. Department of Energy (DOE) 2020 light-duty vehicle system targets [4], regardless of constant effort of decades.

On the basis of the high gravimetric hydrogen capacity of 7.7 wt% and high energy density of 9.9 MJ/kg [5], magnesium, a relative simple system with a low price as well, is a promising candidate for hydrogen storage materials of hydrogen fuel cells [6]. There are, however, still two serious limitations for the practical applications of magnesium hydride: high dehydrogenation tem-

perature and slow hydrogen sorption kinetics [7]. It should be pointed out that the hydrogenation of Mg occurs at a temperature as high as 350–400 °C under a hydrogen pressure of greater than 3 MPa [8]. In order to find feasible magnesium-based hydrogen storage materials, it is crucial to understand their hydrogenation process, which is often divided into several basic steps. The dissociation of hydrogen molecules, the diffusion of hydrogen atoms from surface into bulk, the formation of host metal solid solution dissolved with hydrogen, and finally the transition to metal hydride [9].

Vegge showed that the dissociation and recombination of hydrogen molecules was the rate-limiting processes in adsorption and desorption of hydrogen at the Mg (0001) surface [10]. It should be pointed out that earlier theoretical studies paid attention mostly to the effect of catalysts on the surface dissociation and adsorption of hydrogen. Several approaches have been proposed to overcome the dissociation barrier of hydrogen molecules: catalysts [11], steps [12], defects [13] and tensile strain [14]. We also studied the stability of TMs on Mg (0001) surface and their effects on hydrogen adsorption and found that a combined Ti and Nb co-doping is effective in promoting hydrogen dissociation and adsorption [15]. Dai et al. reported that Al can improve the dehydrogenation properties of MgH₂ system by weakening the interaction between Mg and hydrogen atoms [16]. Magnesium can form Mg–In solid solution alloys through mechanical alloying with indium. Mg (In) solid solution, which can be reversibly formed by

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dehydrogenating from its hydrogenated products, shows lowered reaction enthalpy compared with pure Mg [17].

Nevertheless, the diffusion of hydrogen from surface into bulk interstitial sites is an essential step to form magnesium hydride since the rate-limiting step will become the diffusion of hydrogen through the growing MgH₂ layer once MgH₂ nucleates [18]. Jiang et al. found a stable local H–Mg–H trilayer, a precursor state for Mg hydride [19]. Later on, our study revealed that the biaxial strain remarkably affects the structural stabilities of Mg–H system and found that the formation of the H–Mg–H trilayers is assisted by compressed strains while the following transition to Mg hydride would be helped by tensile strains [20]. We also studied the express penetration of hydrogen on Mg (10 $\bar{1}$ 3) along the close-packed-planes, indicating the crucial role of hydrogen diffusion in Mg hydrogenation [21]. With the repetition and stack of H–Mg–H trilayer structure, the formation of MgH₂ will be favorable. Xin et al. studied the effects of subsurface Mg vacancy on hydrogen trapping property and diffusion of hydrogen, concluding that the diffusion route and barrier of hydrogen atom are hardly affected by the subsurface vacancies [22].

In this paper, we select four typical metal impurities (Ti, Nb, Al, and In) with consideration of their interaction strength with H atoms and have systematically investigated the diffusion of adsorbed hydrogen atoms from surface into bulk magnesium. We reveal that the doped Ti or Nb enhances hydrogen atom diffusion and promotes formation of H–Mg–H trilayer structure, while the doped Al/In does not.

2. Computational method

All our calculations were performed with Vienna Ab initio Simulation Package (VASP) based on the Density Functional Theory (DFT) [23,24]. We used projector augmented wave (PAW) potentials [25,26] to describe the electron–ion interactions, and the generalized gradient approximation (GGA-PBE) [27] was used for the calculation of the exchange–correlation functional. For all calculation, the electron wave function was expanded using plane waves with an energy cutoff of 400 eV. For all of the relaxations, the energy difference of 10^{−4} eV was set as the convergence criterion between successive ionic steps and the forces on each atom were minimized up to 0.01 eV/Å [28].

The optimized lattice constants of bulk Mg of hexagonal structure were $a = 3.19$ Å and $c = 5.21$ Å, and the cohesive energy (E_{coh}) was 1.50 eV/atom in our calculations, in good agreement with the experimental values [29] ($a = 3.21$ Å, $c = 5.21$ Å, and $E_{\text{coh}} = 1.51$ eV/atom) and previous theoretical results [30]. The Mg (0001) surface with four catalysts doped for only single hydrogen adsorption and diffusion was modeled using a 3×3 surface unit cell with six atomic layers. The Brillouin zone of the Mg (0001) surfaces were sampled with a $5 \times 5 \times 1$ k-point mesh following the Monkhorst–Pack scheme [31]. The vacuum space was set to 15 Å to guarantee a sufficient separation between the periodic images along the z direction. Hydrogen and Mg atoms in the top four layers were fully relaxed in the calculations, whereas the bottom two layers were fixed at their bulk configurations. Convergence tests indicated that the cutoff energy and k-point sampling were sufficient to have the energy converged within 1 meV per atom.

The minimum energy path (MEP) for the diffusion and the corresponding diffusion barrier were determined using the climbing image nudged elastic band (CI-NEB) method [32]. For each diffusion path, we selected at least seven images to optimize simultaneously to get the MEP and the migration barrier. The spring constant of 5.0 eV/Å² was used for all diffusion barrier calculations and the force convergence criteria for each atom of images was set to 0.03 eV/Å.

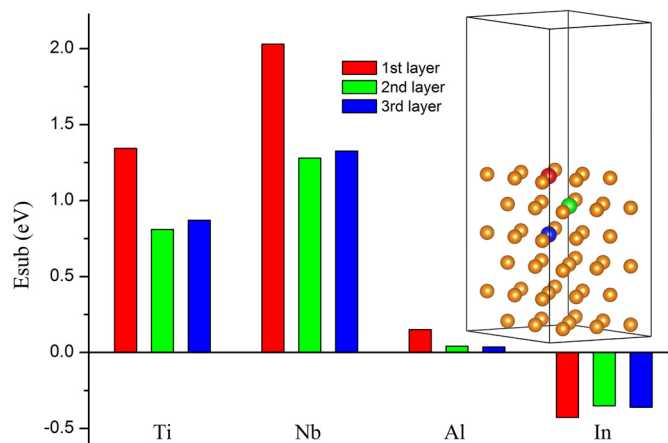


Fig. 1. (Color online.) The substitutional energy of four typical metal impurities (Ti, Nb, Al, and In). The red, green, and blue bar graph represent metal impurities doped in the first, second, and third layers, respectively. The inset graph in the right panel shows the structure of our Mg (0001) surface model.

3. Results and discussions

3.1. Substitutional energy and site preference

First, we have studied the stability of four typical metal impurities substitutions in different layers of Mg (0001). The interstitial sites are not considered for the impurities since Banerjee et al. has reported that these sites are not favored energetically [33]. The substitutional energy for metal impurities doped Mg (0001) surface is defined as:

$$E_{\text{sub}} = E_{\text{M/Mg(0001)}} + E_{\text{Mg}} - E_{\text{M}} - E_{\text{Mg(0001)}}, \quad (1)$$

where $E_{\text{M/Mg(0001)}}$ is the energy of the metal impurities substituted Mg surface, E_{Mg} and E_{M} is the energy of the Mg and metal impurities in the corresponding bulk structures, and $E_{\text{Mg(0001)}}$ is the energy of a clean Mg surface. By definition, a negative E_{sub} value implies that the metal impurities will not segregate from bulk Mg. The calculated E_{sub} values for various metal impurities at different layers of the Mg surfaces are illustrated in Fig. 1.

The negative substitutional energy of In indicate that In is miscible in bulk Mg. This is consistent with the fact that Mg and In will form Mg–In solid solution alloys by mechanical alloying. It is clear that the substitutional energy of Al is a rather small although positive, in line with the fact that Mg–Al compound can also form in experiment and Al can also dissolve in Mg at certain degree. Meanwhile, the other two metals will not form compounds or solid solutions with Mg. By comparing the substitutional energies of different layers, we find that all of the four metal impurities except In prefer to substitute Mg atoms in the inner layers rather than the outmost layer.

The interaction between transition metal impurities and Mg is dominated by the d levels of the metal impurities and the p levels of Mg [15]. When metals without partially filled $3d$ or $4d$ orbitals involved, we may discuss the charge transfer between metal impurities and Mg based on Pauling electronegativity. The Pauling electronegativity of Ti, Nb, and Al are 1.54, 1.60, and 1.61, while In is much stronger, with the value of 1.78. We have calculated the charge density difference of Mg (0001) surface structure alloyed with Ti/In (cf. Fig. 2). Here, $\rho_{\text{diff}} = \rho_{\text{Mg/M}} - \rho_{\text{Mg}} - \rho_{\text{M}}$, and $\rho_{\text{Mg/M}}$, ρ_{Mg} , ρ_{M} stand for the charge corresponding to the metal impurity doped Mg (0001) surface, the doped Mg (0001) surface with the impurity atom removed, and the free impurity atom, respectively. For Ti/In, the charges are transferred from the six nearest neighbor Mg atoms to the doped atoms since the doped impurities are of stronger electronegativity than that of Mg. According to Fig. 2, the

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