Atomic Hydrogen Diffusion in Novel Magnesium Nanostructures: The Impact of Incorporated Subsurface Carbon Atoms

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ABSTRACT. Ab initio Density Functional Theory (DFT) calculations are performed to study the diffusion of atomic hydrogen on a Mg(0001) surface and their migration into the subsurface layers. A carbon atom located initially on a Mg(0001) surface can migrate into the sub-surface layer and occupy a fcc site, with charge transfer to the C atom from neighboring Mg atoms. The cluster of postively charged Mg atoms surrounding a sub-surface C is then shown to facilitate the dissociative chemisorption of molecular hydrogen on the Mg(0001) surface, and the surface migration and subsequent diffusion into the subsurface of atomic hydrogen. This helps rationalize the experimentally-observed improvement in absorption kinetics of H\textsubscript{2} when graphite or single walled carbon nanotubes (SWCNT) are introduced into the Mg powder during ball milling.

1. INTRODUCTION

Magnesium hydride (MgH\textsubscript{2}) is one of the attractive hydrogen storage materials in the automotive industry since it can be directly formed from the reaction of Mg metal with gaseous hydrogen and has a high hydrogen capacity (7.6 weight %) \cite{1-3}. Unfortunately, the application is primarily limited by the high hydrogenation reaction temperature and slow kinetics \cite{4-5}. Experimentally, a number of studies have been devoted to the catalytic effect on hydrogen adsorption of mixing transition metals into the Mg powder by mechanical milling \cite{6-8}. Apart from metallic alloying, some non-metallic elements such as graphitic carbon have been noted to facilitate the activation process of Mg and improve the absorption kinetics of H\textsubscript{2} \cite{9-13}. More recently, a very fast hydrogenation was also observed by using SWCNT instead of graphite in ball milling experiments in our group. However, the possible catalytic mechanism involved when using graphite or SWCNT as additives still remains unclear. Theoretically, \textit{ab initio} DFT calculations have shown considerable predictive power for the analysis of catalytic mechanisms \cite{14-15}. In the process of hydrogenation of Magnesium, hydrogen molecules first dissociate on Mg surface into adsorbed atoms \cite{16-17} and then

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the dissociated atomic H will diffuse into subsurface through fcc channels. To date, the dissociative chemisorption of H₂ onto a clean magnesium surface has been reported by several groups [16-19]. We have recently carried out a preliminary investigation of the effect of incorporated carbon on the dissociative chemisorption of hydrogen [20]. It was shown that a carbon atom located initially on a Mg(0001) surface can migrate into the sub-surface layer and occupy a fcc site, with charge transfer to the C atom from neighboring Mg atoms. The cluster of positively charged Mg atoms surrounding a sub-surface C was then shown to facilitate the dissociative chemisorption of molecular hydrogen on the Mg(0001) surface [ref 20 and below]. However, the effects of subsurface C on the migration of atomic H across the Mg surface and its diffusion into the subsurface layers has not previously been calculated. To further clarify the recent experimental results, however, this is an important objective which we address in the present paper.

In this work, the role of carbon atoms on the diffusion of atomic H on a Mg(0001) surface and into subsurface are studied by ab initio DFT calculations. In order to present a coherent picture, we include relevant results from the recent work [20] as well as the new results on migration and diffusion. The vacuum configuration for a C atom deposited on a Mg(0001) surface is first established. We found [20] that surface C atoms could migrate into the sub-surface and occupy a fcc site. In this work, we utilize the nudged elastic band (NEB) method to compute the Minimum Energy Pathway (MEP) and diffusion barriers for atomic H on a clean Mg(0001) surface, as well as on Mg(0001) surfaces incorporating a finite number (3 and 6) of sub-surface C atoms. Our results indicated a very significant role for C in facilitating diffusion of atomic hydrogen down fcc channels into the subsurface. In the next section we outline our computational method. Section III presents our calculated results and discussion, and the last section is devoted to conclusions.

2. COMPUTATIONAL METHODS

The calculations were performed using the plane-wave basis VASP code [21-22] implementing the generalized gradient approximation (GGA) of PBE exchange correlation functional [23]. An all-electron description, the projector augmented wave method (PAW) [24-25], is used to describe the electron-ion interaction. Using the PAW method, the lattice constant of bulk Mg is calculated to be 3.191 Å, which is only 0.5% in error compared with the experimental value. The bond length of hydrogen molecule in gas phase is calculated to be 0.75 Å and the bond strength is about 4.507 eV, without including zero-point energy (ZPE). These are in good agreement with the experimental results [26]. The cutoff energy used in our calculation for plane waves is chosen to be 500 eV for a very accurate energy calculation. Mg(0001) surface without and with three and six carbon atoms at subsurface are modeled by using a (5×5) unit cell (see Fig.1.a, b, c and d) and only gamma point is used for this calculation. The vacuum space is at least 15 Å, which is enough to guarantee a sufficient separation between periodic images. To determine dissociation barriers and MEP, the NEB method was used [27-28]. This method involves optimizing a chain of images that connect the reactant and product state. Each image is only allowed to move into the direction perpendicular to the hyper-tangent. Hence the energy is minimized in all directions except for the direction of the reaction path. A damped molecular dynamics was used to relax ions until the force in each image are less than 0.02 eV/Å.

3. RESULTS AND DISCUSSIONS

According to other theoretical studies, the atomization energy of graphite and carbon nanotubes is as high as 7.0 eV [29-30]. Mechanical ball milling is, however, a highly energetic process. Hence, it is not surprising that atomic carbon can be produced during ball milling by mixing small amounts of graphite (5%) into the Mg material. To study the vacuum configuration, we first deposited one C atom on either a top or a bridge site at a distance of 1.5 Å from the Mg(0001) surface and optimized the geometry. The relaxation energy for the C atom deposited initially in this way is considerable (e.g. 4.5 eV for on-Top deposition). The final equilibrium configuration was shown in Fig.1.c. The binding
Figure 1. Models used in our calculation. Top view of the relaxed equilibrium configuration for (a) a clean Mg(0001) surface; (b) a Mg(0001) surface with one subsurface C atom; (c) a Mg(0001) surface with 3 subsurface C atoms (c) a Mg(0001) surface with 6 subsurface C atoms. The white and black balls represent Mg and C atoms, respectively.

Figure 2. Contour plots of valence charge difference in (a) XOY plane and (b) XOZ plane containing subsurface C and neighboring Mg atoms. (c) and (d) are 3D iso-surface plots of valence electron charge density difference, which show charge accumulation (0.75 electron/Å$^3$) on subsurface C atom and charge depletion (-0.15 electron/Å$^3$) from neighboring Mg atoms, respectively.

energy ($E_b$) for C incorporated into Mg subsurface is calculated by

$$E_b = E_{Mg(0001)+C} - E_{Mg(0001)} - E_c$$  \hspace{1cm} (I)

Where $E_{Mg(0001)+C}$, $E_{Mg(0001)}$, and $E_c$ represent the total energy of Mg(0001) surface with a subsurface carbon atom, clean Mg(0001) surface and an isolated carbon atom. The $E_b$ is calculated to be 7.16 eV, which implies sufficiently positive segregation energy to be required to move a solute atom from the
Figure 3. Energy profiles for the migration of atomic H from hcp to fcc site (IS→IMS) on Mg(0001) surface with zero (Solid line with squares), three (dashed line with spheres) and six (dotted line with triangles) sub-surface carbon atoms, respectively.

bulk to the surface of the host metal [15]. In this case, the C atom can migrate into the sub-surface and finally occupies a fcc site. In order to gain more insight for the equilibrium configuration containing a subsurface carbon, the valence charge electron density difference ($\rho_{\text{diff}}$) in vacuum space is analyzed by the following equation and plotted in Fig.2.

$$\rho_{\text{diff}} = \rho_{\text{Mg(0001)+C}} - \rho_{\text{Mg(0001)}} - \rho_{C}$$

Here $\rho_{\text{Mg(0001)+C}}$, $\rho_{\text{Mg(0001)}}$, and $\rho_{C}$ represent the valence charge density for Mg(0001) surface with a subsurface carbon atom, clean Mg(0001) surface and an isolated carbon atom having the same position as the subsurface carbon. It can be seen clearly that there is charge accumulation on the subsurface C atom and charge depletion from neighboring Mg atoms. This indicates a significant charge transfer between them. Additionally, charge analysis was also performed for the equilibrium configuration by voronoi partitioning [31]. The amount of charge transfer is about 1.0 electron from neighboring Mg atoms to the sub-surface C atom.

The hydrogenation of Magnesium involves molecular hydrogen dissociating on the Mg surface in the first step, followed subsequently by diffusion of the dissociated H atoms into the subsurface fcc sites through the fcc channels [17,32]. The former process in the presence of incorporated sub-surface carbon has been characterised for the first time in our previous work [20]. The ensuing question is whether the sub-surface C atom will also affect the dynamic diffusion of atomic H across the Mg(0001) surface and into subsurface. As shown in ref. [17,32], the most plausible diffusion pathway is the diffusion of atomic H from an hcp to a fcc site on the Mg(0001) surface and then to the subsurface fcc site. To explore this process in the presence of incorporated carbon, a series of NEB calculations were performed to obtain the MEP and the activation barrier for the diffusion of atomic hydrogen on Mg(0001) surface and into subsurface both with no carbon, with three sub-surface carbon atoms and with six sub-surface C atoms (see Fig.1a, Fig.1c and Fig.1d). Three special configurations with one atomic H on surface hcp, fcc and subsurface fcc sites are chosen to be the initial state (IS), intermediate state (IMS) and final state (FS), respectively. They are first optimized separately with the conjugate gradient method. Then two chains of images linking the IS-IMS and IMS-FS sites are chosen to be the initial state (IS), intermediate state (IMS) and final state (FS), respectively. They are first optimized separately with the conjugate gradient method. Then two chains of images linking the IS-IMS and IMS-FS sites are chosen to be the initial state (IS), intermediate state (IMS) and final state (FS), respectively. They are first optimized separately with the conjugate gradient method. Then two chains of images linking the IS-IMS and IMS-FS sites are chosen to be the initial state (IS), intermediate state (IMS) and final state (FS), respectively. They are first optimized separately with the conjugate gradient method.
Mg(0001) surface. Fig. 4 presents the energy profiles for the diffusion of H atom from a surface fcc site downward to a subsurface fcc site (IMS→FS). The activation barrier are 0.47 eV, 0.14 eV and 0.08 eV for the case of pure Mg(0001) surface, Mg(0001) surface with 3 and 6 subsurface carbon atoms, respectively. It is apparent from the results in Figs. 3 and 4 that sub-surface C atoms can not only facilitate advantageous positioning of H atoms on the surface subsequent to dissociation, but can also promote a “funneling” effect – facilitating diffusion of atomic H into the subsurface by lowering the activation barriers to transport down the encircled fcc channels. This effect may be attributed to the decreased electron repulsion between the diffusing H atom and its neighboring Mg atoms in the surface layer due to the charge transfer effects alluded to above. The present results on atomic H diffusion in the presence of incorporated carbon hence further support and rationalise the experimentally-observed improvement in absorption kinetics of hydrogen when graphite or SWCNT is introduced into the Mg material during ball milling.

**Figure 4.** Energy profiles for the diffusion of atomic H from surface fcc downward to a subsurface fcc site (IMS→FS) with zero (Solid line with squares), three (dashed line with spheres) and six (dotted line with triangles) preoccupied carbon atoms at subsurface, respectively.

### 4. CONCLUSIONS

In summary, *ab initio* Density Functional Theory (DFT) calculations are performed to study the diffusion of hydrogen atom on a Mg(0001) surface and their migration into the subsurface layers. We found in our earlier work [20] that a C atom on a Mg(0001) surface could migrate into the sub-surface and occupy a fcc site. Charge will be transferred to the sub-surface C atom from the neighboring Mg atoms. The cluster of positively charged Mg atoms surrounding sub-layer C atoms not only facilitates the dissociative chemisorption of molecular hydrogen on the Mg(0001) surface [20], but additionally is found in this work to have a dramatic enhancement effect on the surface migration and subsequent diffusion of atomic hydrogen into the sub-surface layers. Our present results further support and help rationalize the experimentally-observed improvement in absorption kinetics of H₂ when graphite or single walled carbon nanotube (SWCNT) are introduced into the Mg powder during ball milling.

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