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# Effects of Li on hydrogen absorption properties of $Mg_{17}Al_{12}(110)$ surface: A density functional theory study

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## ABSTRACT

On the basis of density functional theory (DFT), the catalytic effects of Li on hydrogen absorption properties of the  $Mg_{17}Al_{12}(110)$  surfaces are studied. The Li-containing  $Mg_{17}Al_{12}(110)$  surfaces were composed of the Li-substituted and Li-adsorbed systems, namely  $Mg_{16}LiAl_{12}(110)$  and  $Mg_{17}Al_{12}(110)/Li$  surfaces, respectively. Calculations indicate that adsorption energies of H ( $H_2$ ) on the  $Mg_{17}Al_{12}(110)$  surfaces with a low amount of Li were significantly improved relative to hydrogen on the clean surface. Especially, the energy of H ( $H_2$ ) on the  $Mg_{17}Al_{12}(110)/Li$  system was  $-0.68$  ( $-0.48$ ) eV. Moreover, the addition of Li remarkably promotes the dissociative properties of  $H_2$  on the (110) surface. The barrier energy of  $H_2$  dissociation on the  $Mg_{17}Al_{12}(110)/Li$  surface was 0.14 eV, which was much lower than that (0.87 eV) on the pure surface. Analysis of electronic structures reveals that the H-s orbital hybridized with the Mg-s evidently in the Li-containing systems. The formation of Li–H bond and the interaction between  $H_2$  and Li atom may explain the enhanced hydrogenation properties of  $Mg_{17}Al_{12}(110)/Li$  surface.

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## Introduction

Researchers are studying various ways to store hydrogen due to hydrogen is a clean energy carrier [1–6]. Among the available ways of hydrogen storage, the method of forming metal hydride is considered to be more safe, efficient, and accurate.  $MgH_2$  has attracted extensive attention because its hydrogen storage capacity is up to 7.6 wt.%. Scientists have found that adding Al to  $MgH_2$  improves the hydrogen storage performances of materials. Mg–Al alloy is a kind of solid state hydrogen storage materials. Its intermetallic compound,

$Mg_{17}Al_{12}$ , have been employed to store hydrogen [7–16]. Andraesen et al. [10] have studied three phases ( $\beta$ - $Mg_2Al_3$ ,  $\gamma$ - $Mg_{17}Al_{12}$  and  $\epsilon$ ) of Mg–Al alloy and reported that the hydrogen storage performance of  $\gamma$ - $Mg_{17}Al_{12}$  was higher than the other two phases by comparing their hydrogen storage capacity, thermodynamic and kinetic properties. It's observed that the enthalpy of hydride formation of magnesium was reduced upon alloying with Al due to a slightly endothermic disproportionation reaction. Furthermore, the kinetics of hydrogenation as well as dehydrogenation could be significantly improved by alloying compared to pure Mg. The expense of these improvements in the (de-) hydrogenation properties

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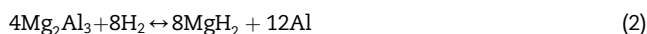
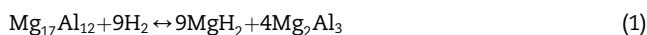
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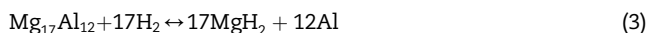
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was a lower gravimetric hydrogen density in the hydrogenated product.

In experiments, Bouaricha et al. [7] have found that when Mg:Al ratio was 58:42, there was only one nanocrystalline  $Mg_{17}Al_{12}$  intermetallic phase, which led to the formation of  $MgH_2$  and Al after hydrogen absorption. The reaction was completely reversible that  $Mg_{17}Al_{12}$  was recovered after desorption. Following, Zhang et al. [8] have investigated that the  $Mg_{17}Al_{12}$  compound reacted with hydrogen to form  $Mg_2Al_3$ ,  $MgH_2$  and Al at 573K. Then, when the hydrogenation temperature raised to 623K,  $Mg_2Al_3$  decomposed into  $MgH_2$  and  $Al_{0.9}Mg_{0.1}$ , the hydrogen storage capacity was 4.03 wt.%. Next, Yabe et al. [9] have revealed that  $Mg_{17}Al_{12}$  was able to absorb hydrogen up to 3.2 wt.% at 5.3 MPa, and was also able to desorb hydrogen at 523 K. In all, the related reaction equations of hydrogenation reaction for  $Mg_{17}Al_{12}$  are as follows:



Recently, we have prepared  $Mg_{17}Al_{12}$  alloy by sintering, liquid nitrogen quenching and ball milling [13]. The maximum hydrogen storage capacity was 4.0 wt.%, which is in agreement with the theoretical value (4.4 wt.%). In addition, the hydrogenation reactions have been simplified that there was no  $Mg_2Al_3$ , and the procession can be described as follow:



However, the (de-) hydrogenation kinetics of  $Mg_{17}Al_{12}$  haven't reached human's expectation. Experimentally, various catalysts (e.g., transition metal (TM) [15,17–20] have been added into Mg–Al alloy to improve its hydrogen properties. Lee et al. [20] have discussed the effect of X wt.% Ni (X = 0, 10, 20) on the  $Mg_{17}Al_{12}$  alloy. Their x-ray diffraction (XRD) results showed that there were stable  $Al_3Ni$  and  $Al_3Ni_2$  phases after hydrogenation and surplus Mg beyond desorption. Following, we have prepared  $Mg_{17}Al_{12}+TM$  (TM = Ti, V, Ni) by using sintering and ball milling methods [15]. It's found that both the hydrogenation and dehydrogenation temperatures of the Mg–Al alloy dropped after the addition of TM. Especially, Mg–Al–V alloy began to desorb hydrogen at 244 °C, while the Mg–Al alloy was 310 °C, and the activation energy of the former was 34.6 kJ mol<sup>-1</sup> lower than that of the later.

For light metal, Li is also used as a catalyst to improve the hydrogenation performance of Mg–Al alloys [19,21–23]. As the lightest metal, Li can store hydrogen, the hydrogen capacity of Li is 12.5 wt.%. In experiments, we have prepared the  $Mg_{17}Al_{12}(Li)$  alloy by sintering, annealing, and ball milling [22]. The hydrogen storage capacity of the  $Mg_{17}Al_{12}(Li)$  was 3.7 wt.%, and its dehydrogenation enthalpy was as low as 53 kJ mol<sup>-1</sup> H<sup>-2</sup>. Zhang et al. [21] have obtained Mg–Li–Al–H complex hydride by mechanochemical synthesis. Their results showed that the higher hydrogen desorption rate and the larger hydrogen released amount were consulted in a low temperature range when the Li/Al ratio was lower.

In this paper, the effects of Li on hydrogen absorption properties of  $Mg_{17}Al_{12}(110)$  surface are revealed by using the DFT method. The structures and energies of hydrogen adsorption and dissociation on the (110) surfaces are studied.

Furthermore, the related electronic structures including electric density and density of states are discussed.

## Calculation methods and models

All calculations used in this paper were done in the Cambridge serial total energy package (CASTEP) [24]. The exchange correlation potential was used by Perdew-Burke-Ernzerhof (PBE) [25] function within the generalized gradient approximation (GGA) methods [26–28]. The cutoff energy of plane wave was set at 330 eV. The convergence threshold for the maximum energy change, the maximum force, the maximum stress and the maximum displacement were  $2 \times 10^{-5}$  eV/atom, 0.05 eV/Å, 0.1 Gpa, and 0.002 Å, respectively. In our calculations, a  $6 \times 6 \times 6$  Monkhorst-Pack [29] k-point grid for the  $Mg_{17}Al_{12}$  bulk structure and a  $6 \times 6 \times 1$  k-point grid for the  $Mg_{17}Al_{12}(110)$  surface were employed. Moreover, the Grimme method for DFT-D correction [30] was added to the  $Mg_{17}Al_{12}(110)$  surface on the basis of the original calculation methods. For searching the pathways of H<sub>2</sub> dissociation on the Li-containing surfaces, the complete linear synchronous transit (LST) and quadratic synchronous transit (QST) [31] with the conjugate gradient (CG) [32] methods were employed.

For the bulk material,  $Mg_{17}Al_{12}$  ( $I\bar{4}3m$ , space group No.217) alloy is a body-centered cubic structure. Mg atoms occupy Wyckoff points 2a (0, 0, 0), 8c (0.3244, 0.3244, 0.3244) and 24 g (0.35622, 0.35622, 0.03925), the Wyckoff positions of Al atoms are 24 g (0.08996, 0.08996, 0.27681). The three different points of Mg atoms are labeled as Mg1, Mg2, Mg3, respectively, as showed in Fig. 1(a). In our models, there are 34 Mg atoms and 24 Al atoms in a unit cell of the  $Mg_{17}Al_{12}$  alloy.

For the Li-containing surfaces, the  $Mg_{17}Al_{12}(110)$  surfaces consisted of the Li-adsorbed and Li-substituted surfaces are considered. Fig. 1(b) shows that the supercell of  $Mg_{17}Al_{12}(110)$  surface was divided into three layers, and the thickness of the vacuum layer was set to 15 Å. The models of surfaces used in our calculations contain 17 Mg atoms and 12 Al atoms. All adsorbates and atoms located at the 1st layer were relaxed as shown in Fig. 1(b), and the remaining atoms are fixed to simulate the bulk structures.

To obtain stable Li-substituted surfaces, the Mg and Al atoms labeled as Mg1, Mg2, Mg3,  $Al_{sur}$ ,  $Al_{sub1}$  and  $Al_{sub2}$  in the relaxed layer was replaced by Li, respectively, as shown in Fig. 1(c). Besides, for the Li-adsorbed systems, we consider 13 sites for the adsorbates adsorption, which contain the top sites of the Mg1, Mg2, Mg3,  $Al_{sur}$ ,  $Al_{sub1}$  and  $Al_{sub2}$  in the relaxed plane (namely a-f), and the bridge sites of long bond of Mg1–Mg2 as well as the short bonds of Mg1–Mg2, Mg2–Mg3, Mg1–Mg3,  $Al_{sur}$ – $Al_{sur}$ , Mg3–Mg3 and  $Al_{sur}$ –Mg3 (namely f-m), as shown in Fig. 1(d).

Zhou et al. [33] have defined the adsorption energy  $E_{ads}$  (the smaller the value, the better the adsorption property) as the energy difference before and after adsorption.  $E_{ads}$  of Li (H and H<sub>2</sub>) on the  $Mg_{17}Al_{12}(110)$  surfaces is described as follows:

$$E_{ads} = (E_{surface/adsorbate} - E_{surface} - N \times E_{adsorbate}) \quad (4)$$

Where  $E_{surface/adsorbate}$  is the energy of the system after adsorption,  $E_{surface}$  is the energy of the clean or the Li-

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