Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Hydrogen penetration and diffusion on $Mg_{17}Al_{12}$ (110) surface: A density functional theory investigation

Ziyan Zhang [a], *Xingyu Zhou* [a], *Hongliang Zhang* [a], *Jin Guo* [a,b], *Hua Ning* [a,b,*]

[a] *Guangxi Key Laboratory for Relativistic Astrophysics, Guangxi Colleges and Universities Key Laboratory of Novel Energy Materials and Related Technology, College of Physics Science and Technology, Guangxi University, Nanning 530004, PR China*

[b] *Guangxi Collaborative Innovation Center of Structure and Property for New Energy and Materials, School of Material Science and Engineering, Guilin University of Electronic Technology, Guilin, 541004, PR China*

ARTICLE INFO

Article history:
Received 4 July 2017
Received in revised form
20 August 2017
Accepted 24 August 2017
Available online 14 September 2017

Keywords:
Density functional theory
Hydrogen storage
Adsorption
Penetration
Mg-Al alloy

ABSTRACT

The adsorption, diffusion and penetration of H on the $Mg_{17}Al_{12}$ (110) surface are investigated systematically by means of the density functional theory calculations. Results indicate that H and H_2 prefer to adsorb on the Mg-Mg bridge sites of the $Mg_{17}Al_{12}$ (110) surface. The lowest barrier energy of molecular hydrogen dissociation on the (110) surface is ~0.87 eV. The penetration processes of atomic hydrogen incorporation into the $Mg_{17}Al_{12}$ (110) surface are discussed. It is obtained that the H penetrates from the $Mg_{17}Al_{12}$ (110) surface into the subsurface with the minimum barrier of ~0.63 eV, while the hydrogen atom spreads into the deeper $Mg_{17}Al_{12}$ (110) surface with lower barrier.

Introduction

As lightweight materials with high hydrogen storage capacity, nontoxic, low cost, and convenient synthesis, Mg-based alloys have been investigated widely in the field of hydrogen fuel cells and hydrogen storage. However, the poor thermodynamic and kinetic performance of the magnesium hydride limits the practical environmental application. Experiments reported that aluminum composes the main alloying element to improve the hydrogen storage properties of magnesium alloys, providing enhanced the hydrogenation rate, reduced the dehydrogenation temperature, and weakened the thermal stability et al. [1–10]. In Mg-Al alloys, $Mg_{17}Al_{12}$ is a dominant intermetallic phase, its theoretical hydrogen storage capacity is 4.4 wt%. Recently, we have studied that in the process of hydrogenation and dehydrogenation, Mg-Al alloy reaction with hydrogen can be regulated as a one-step reversible reaction by ball-milling, sintering, and quenching [11]. The

* *Corresponding author*. College of Physics Science and Technology, Guangxi University, Nanning, PR China.
E-mail address: ninghua@gxu.edu.cn (H. Ning).

http://dx.doi.org/10.1016/j.ijhydene.2017.08.176

related reversible hydrogenation reaction can be described as $Mg_{17}Al_{12} + H_2 \leftrightarrow MgH_2 + Al$.

According to our understanding, few theoretical investigations of hydrogen reaction with Mg-Al alloy have been reported. Recently the dissociation and incorporation of H on (in) $Mg_{17}Al_{12}$ (100) surface have been investigated [12]. The adsorption energies, dissociation barriers, and penetration pathways of H (H_2) on the (100) surface were discussed by the density functional theory (DFT) method. Xiao et al. [13] have reported that the surface energy of $Mg_{17}Al_{12}$ (110) surface is lower than that of $Mg_{17}Al_{12}$ (100) surface, suggesting that the (110) surface is more steady than the (100) surface. Moreover, in experiments, the X-ray diffraction (XRD) analysis reveals that the amount of $Mg_{17}Al_{12}$ (110) surface is larger than that of $Mg_{17}Al_{12}$ (100) surface [14]. Thus, the aim of this work is to explore the hydrogenation process of $Mg_{17}Al_{12}$ alloy comprehensively. The quantitative calculations of hydrogen adsorption on the $Mg_{17}Al_{12}$ (110) surface and the pathways of hydrogen dissociation and penetration on (in) the surface have been carried out. We expect that the results can be used to study the effect of catalysts on the hydrogen storage material of Mg-Al alloy in the near further.

Computational details

All density functional theory calculations in this study were performed on the CASTEP program [15] from Materials Studio software. We used a 330 eV kinetic energy cutoff and $6 \times 6 \times 6$ ($6 \times 6 \times 1$) k-point mesh for bulk (surface) simulations. The Perdew, Burke, Ernzerhof (PBE) and generalized gradient approximation (GGA) were used for the exchange correlation potential [16–18]. For the $Mg_{17}Al_{12}$ (110) surface, the model was built using a supercell with 29 atoms, consisting of 17 Mg atoms and 12 Al atoms. The vacuum spacing between the neighboring slabs was selected as 15 Å. Along the super-cell z axis, there are seven atomic planes in the $Mg_{17}Al_{12}$ (110) surface, the top two atomic planes (seen in Fig. 1(b)) and the adsorbates were relaxed to simulate the approximate surface conditions, while the remaining atomic planes were fixed, playing a role of bulk alloy. More than two atomic planes (up to four outmost planes) of the $Mg_{17}Al_{12}$ (110) surface were free to relax. Calculations show that there are tiny differences between the various optimized surfaces in total energies, in which the energy of the surface with relaxing the outmost two planes is the minimum. In adsorption calculations, to obtain the correct interfacial properties, we considered the dispersion corrected DFT (DFT-D) with Grimme type [19]. In hydrogen incorporation calculations, all atoms were relaxed in the whole systems. For the optimized structures, the convergence criteria was as follows: 1×10^{-5} eV for energy change, 1×10^{-3} eV/Å for maximum displacement, 0.03 eV for residual force, and 0.05 GPa for maximum stress. In addition, the linear synchronous transit (LST) calculations and quadratic synchronous transit (QST) [20] with conjugate gradient (CG) methods [21] were used to gain the barriers energies and transition states (TS) of hydrogen dissociation and incorporation on (in) the $Mg_{17}Al_{12}$ (110) surfaces.

The adsorption energies (E_{ads}) of H and H_2 on the $Mg_{17}Al_{12}$ (110) surfaces were calculated as:

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

where N is the number of absorbates, $E_{surface/adsorbate}$ are the total energies of total systems, $E_{surface}$ is the total energy of the $Mg_{17}Al_{12}$ (110) surface. $E_{adsorbate}$ are the total energies of $\frac{1}{2}$ H_2 and H_2, respectively. The positive energy of E_{ads} demonstrates the endothermic process of hydrogen on the $Mg_{17}Al_{12}$ (110) surface, while the negative energy of E_{ads} indicates the exothermic process.

Results

Structure of the $Mg_{17}Al_{12}$ (110) surface

The unit cells of bulk $Mg_{17}Al_{12}$ and $Mg_{17}Al_{12}$ (110) surface are presented in Fig. 1. The lattice parameters of $Mg_{17}Al_{12}$ alloy as well as the surface energies of $Mg_{17}Al_{12}$ (100) and (110) surfaces are derived and listed in Table 1. For $Mg_{17}Al_{12}$ alloy, the Mg atoms locate at the 2a, the 8c, and the 24 g positions, marked by Mg1, Mg2, and Mg3, respectively, and the Al atoms

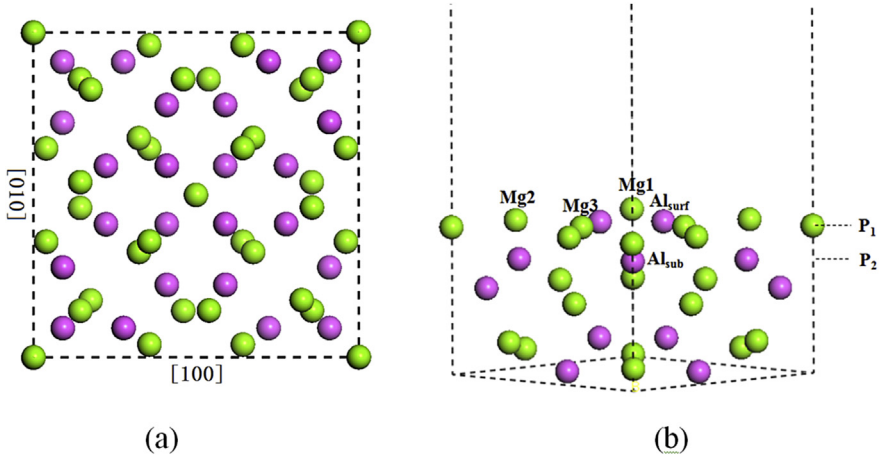

Fig. 1 – Structures of (a) $Mg_{17}Al_{12}$ alloy and (b) the $Mg_{17}Al_{12}$ (110) surface.