



Prediction of the electronic structures, thermodynamic and mechanical properties in manganese doped magnesium-based alloys and their saturated hydrides based on density functional theory



Ziying Zhang^{a,*}, Huizhen Zhang^b, Hui Zhao^a, Zhishui Yu^a, Liang He^a, Jin Li^c

^a School of Materials Engineering, Shanghai University of Engineering Science, Shanghai 201620, China

^b School of Management, University of Shanghai for Science and Technology, Shanghai 200093, China

^c Department of Materials Science, Fudan University, Shanghai 200433, China

HIGHLIGHTS

- Mn-doping reduced the lattice parameters of Mg₂Ni alloy and its hydride.
- Mn-doping weakened the stabilities of Mg₂Ni alloy and its hydride.
- A new Mg₃MnNi₂ intermetallic formed in Mn-doped Mg₂Ni alloys.
- The charge/discharge cycles of Mg₂Ni was improved by giving enough doping content.

ARTICLE INFO

Article history:

Received 25 September 2014

Received in revised form

23 December 2014

Accepted 16 January 2015

Available online 17 January 2015

Keywords:

Hydrogen storage alloy

Density functional theory

Electronic structure

Thermodynamic instability

Elastic properties

ABSTRACT

The crystal structures, electronic structures, thermodynamic and mechanical properties of Mg₂Ni alloy and its saturated hydride with different Mn-doping contents are investigated using first-principles density functional theory. The lattice parameters for the Mn-doped Mg₂Ni alloys and their saturated hydrides decreased with an increasing Mn-doping content because of the smaller atomic size of Mn compared with that of Mg. Analysis of the formation enthalpies and electronic structures reveal that the partial substitution of Mg with Mn reduces the stability of Mg₂Ni alloy and its saturated hydride. The calculated elastic constants indicate that, although the partial substitution of Mg with Mn lowers the toughness of the hexagonal Mg₂Ni alloy, the charge/discharge cycles are elevated when the Mn-doping content is high enough to form the predicted intermetallic compound Mg₃MnNi₂.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

With the increasing demand for environmentally friendly energy technologies, hydrogen has received increasing interest over the past decades [1–4]. However, the large-scale application of hydrogen as a fuel is dependent on the ability of its storage materials, where large gravimetric and volumetric densities are required to safely and economically store hydrogen under ambient conditions [5–7]. Magnesium-based alloy (Mg₂Ni) as a hydrogen storage material is promising owing to its high capacity, good safety, low cost, relatively established preparation technologies and good

reversibility [8–11]. However, the practical use of Mg₂Ni alloy in storing hydrogen is limited because of its poor hydriding/dehydriding kinetics and the high thermodynamic stability of Mg₂Ni hydride (Mg₂NiH₄) [12–14]. To improve the dehydrogenation properties of Mg₂Ni hydride, the design of Mg_{2-x}M_xNi or Mg₂Ni_{1-x}M_x ternary compounds by the substitution of Mg or Ni with a third component (M) has been studied. The experimental and theoretical results showed that the partial substitution of Mg or Ni with third elements altered the structural stabilities of Mg₂Ni and saturated Mg₂Ni hydride, modifying the hydrogen desorption enthalpy (ΔH_{des}) of Mg₂Ni hydride [14–22].

Recently, Mn was experimentally added to Mg₂Ni to improve its hydrogen storage properties [23–25]. The experimental results indicated that, although the electrochemical properties of Mg₂Ni and its saturated hydride were improved by different degrees after

* Corresponding author.

E-mail address: zzying@uses.edu.cn (Z. Zhang).

doping with Mn, no consensus has yet been reached on the substitution of the Mg or Ni lattice sites in Mg_2Ni alloy because of the different substitution methods used. Tsushio et al. [26] proposed that the substitution of Mn for Ni needs to be considered first, while Huang et al. [27] found that $Mg_2Ni_{1-x}Mn_x$ alloys transformed into a Ni-enriched Mg_3MnNi_2 phase when the Mn content reached 0.375, after giving the sample enough ball-milling time. Furthermore, they also reported that the most preferable site for the substitution of Mn in the Mg_2Ni lattice was theoretically confirmed to be the Mg (6i) lattice site after the formation enthalpy of Mg_2Ni alloy was calculated, where the atoms at the Mg (6f), Mg (6i), Ni (3b) and Ni (3d) lattice sites were each replaced with one Mn atom [28]. It is therefore of interest to theoretically investigate the effect of the Mn-doping content on the electronic structure, thermodynamic and mechanical properties of Mg_2Ni alloy and its saturated hydride. This study not only contributes to understanding the mechanism of Mn doping in Mg_2Ni alloy and its saturated hydride, but also provides guidance on exploring novel hydrogen storage materials with improved hydrogen storage characteristics. However, no reports have shed light on this issue to date.

Here, the crystal structures, electronic structures, thermodynamic and mechanical properties of Mg_2Ni alloy and its saturated hydride are investigated with different Mn-doping contents, using first-principles density functional theory (DFT) calculations. The evolution of the lattice parameters of Mg_2Ni alloy and its saturated hydride with an increasing Mn-doping content is presented. The stabilities of Mn-doped Mg_2Ni alloys and their saturated hydrides are discussed in detail. The formation of a new Mg_3MnNi_2 intermetallic compound and an improved charge/discharge life cycle are predicted after enough Mn-doping content has been added to the sample.

2. Calculation models and method

Mg_2Ni alloy has a hexagonal structure, belonging to the P6222 space group (No. 180) with lattice parameters $a = 5.219 \text{ \AA}$ and $c = 13.293 \text{ \AA}$ [29]. Each unit cell contains six formula units,

expressed as $Mg_{12}Ni_6$. The 12 Mg atoms occupy the 6f and 6i lattice sites, while the six Ni atoms occupy the 3b and 3d lattice sites. At ambient temperature, the structure of Mg_2NiH_4 was monoclinic with the space group C2/C (No. 15), containing 16 Mg atoms, eight Ni atoms and 32 H atoms [30]. The unit cell for Mg_2Ni and the primitive cell for Mg_2NiH_4 are shown in Fig. 1(a) and (b). The substitution of Mg with Mn in Mg_2Ni and Mg_2NiH_4 was carried out according to the designed compositions, $Mg_{2-x}Mn_xNi$ and $Mg_{2-x}Mn_xNiH_4$ ($x = 0, 0.25$ or 0.5). This means that 0, 1.5 or 3 Mn atoms were introduced to substitute 0, 1.5 or 3 Mg atoms at the 6i lattice site in the Mg_2Ni unit cell, while 0, 1 or 2 Mg atoms were substituted by Mn atoms in the Mg_2NiH_4 primitive cell. To have 1.5 Mg atoms in the Mg_2Ni unit cell substituted with 1.5 Mn atoms, an equivalent treatment to replace three of the 24 Mg atoms in the Mg_2Ni ($2 \times 1 \times 1$) supercell was carried out to achieve a doping level of $x = 0.25$ in $Mg_{2-x}Mn_xNi$. Fig. 2a shows the structure of the unit cell for the Mg_3MnNi_2 phase, which has cubic symmetry (space group Fd-3m) with $a = 11.564 \text{ \AA}$ [28]. The Mg_3MnNi_2 unit cell contained 16 formula units of Mg_3MnNi_2 , namely $Mg_{48}Mn_{16}Ni_{32}$. Forty-eight Mg atoms, 16 Mn atoms and 32 Ni atoms occupied the Mg (48f), Mn (16d) and Ni (32e) lattice sites, respectively. Fig. 2b shows the Mg_3MnNi_2 primitive cell with 12 Mg atoms, four Mn atoms and eight Ni atoms, used in the calculation to increase the computational efficiency. All calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) [31], which is a first-principles plane wave pseudopotential method based on DFT. Ultrasoft pseudopotentials [32] in reciprocal space were used. The Perdew Burke Ernzerhof (PBE) functional in the generalized gradient approximation (GGA) [33] was adopted as the exchange-correction functional. The crystal reciprocal-lattices were integrated over the symmetrized Brillouin zone by summing over the special k-points that were generated using the Monkhorst-Pack scheme [34]. $6 \times 6 \times 2$ and $2 \times 4 \times 4$ special k-point meshes were employed for $Mg_{2-x}Mn_xNi$ and $Mg_{2-x}Mn_xNiH_4$ ($x = 0, 0.25, 0.5$). A plane wave cut-off energy of 340 eV was used for all cases to ensure the calculations converged for the total energies and forces acting on the atoms. A finite basis set correction and the Pulay

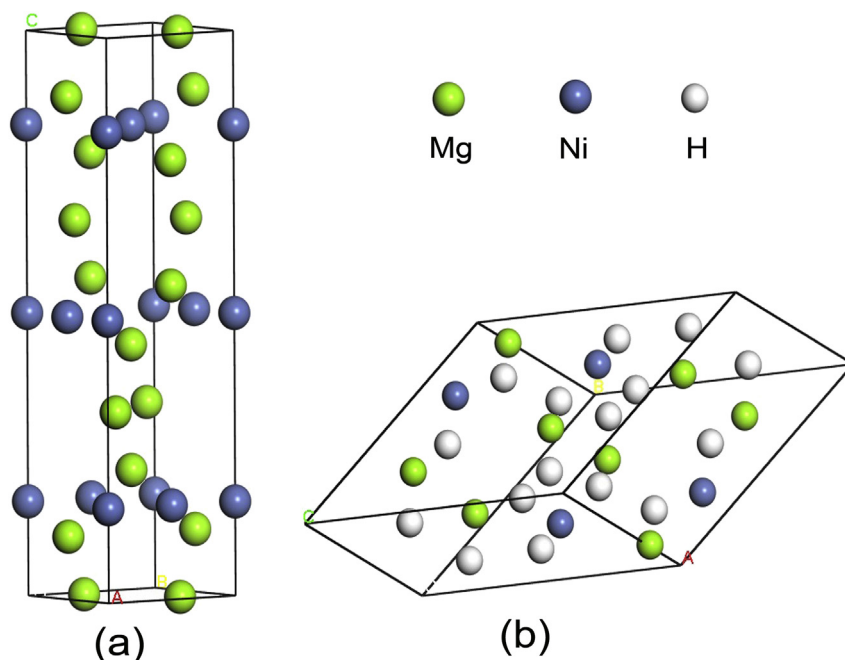


Fig. 1. Unit cell of Mg_2Ni (a) and primitive cell of Mg_2NiH_4 (b).

Download English Version:

<https://daneshyari.com/en/article/7733369>

Download Persian Version:

<https://daneshyari.com/article/7733369>

[Daneshyari.com](https://daneshyari.com)