



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Synthesis of Mg_2FeD_6 under low pressure conditions for Mg_2FeH_6 hydrogen storage studies

Anna-Lisa Chaudhary ^{a,*}, Sascha Dietzel ^b, Hai-Wen Li ^{c,d}, Etsuo Akiba ^{c,d}, Nils Bergemann ^a, Claudio Pistidda ^a, Thomas Klassen ^{a,b}, Martin Dornheim ^a

^a Department of Nanotechnology, Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Max-Planck Strasse 1, D-21502 Geesthacht, Germany

^b Department of Mechanical Engineering, Helmut Schmidt University, Holstenhofweg 85, D-22043 Hamburg, Germany

^c Faculty of Engineering, Mechanical Engineering, Kyushu University, Fukuoka, Japan

^d International Institute for Carbon-Neutral Energy Research (WPI-I2CNR), Kyushu University, Fukuoka, Japan

ARTICLE INFO

Article history:

Received 8 December 2016

Received in revised form

1 February 2017

Accepted 3 February 2017

Available online xxx

Keywords:

Hydrogen storage

Magnesium iron deuteride

Magnesium iron hydride

Complex hydrides

Low pressure

ABSTRACT

Mg_2FeD_6 is successfully synthesised with various degrees of purity using reactive ball milling and annealing under low pressure deuterium conditions to a maximum of 10 bar. The deuteride of the low cost ternary metal hydride Mg_2FeH_6 , is synthesised to enable further characterisation studies such as isotopic exchange behaviour. Both on laboratory and industrial scales, keeping the pressure low reduces the need for expensive compression systems and also minimises the quantity of gas necessary for use; therefore it is important to assess synthesis under these cost effective conditions. This is especially the case when using a specialised gas such as high purity deuterium. The maximum pressure chosen is 10 bar, to comply with the High Pressure Safety Act in Japan. This Safety Act limits the use of any gas including hydrogen and deuterium to 10 bar eliminating the use of traditional synthesis methods for Mg_2FeH_6 or Mg_2FeD_6 synthesis at high pressure (120 bar). Ball milling parameters such as milling times, ball to powder ratios as well as sintering times were altered to achieve improved Mg_2FeD_6 yields under these low pressure conditions.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Solid state hydrogen storage materials are of increasing interest for the development of complete clean green energy and storage systems. In particular, intermittent renewable energy production from the most common sources such as solar or wind, can produce hydrogen from water during times

of excess load, then stored to be used with a fuel cell system at times of low production. This then allows continuous supply of energy independent of renewable source availability. Storing hydrogen as a solid within a metal matrix is a cost effective method of hydrogen storage without the need for compressing or liquefying hydrogen in the traditional storage method sense. One example of this metal matrix is the low cost ternary metal hydride Mg_2FeH_6 . This material has octahedral

* Corresponding author. Fax: +49 4152 87 2636.

E-mail address: anna-lisa.chaudhary@hzg.de (A.-L. Chaudhary).

<http://dx.doi.org/10.1016/j.ijhydene.2017.02.033>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

coordination of Fe by hydrogen forming a FeH_6^{4-} anion that is surrounded by eight Mg^{2+} in a cubic K_2PtCl_6 structure type configuration [1,2]. Mg_2FeH_6 is stable and reversible for more than 500 cycles [3] with a storage capacity of hydrogen up to 5.47 wt. % and several publications have stated that this material has a standard formation enthalpy of 98 ± 3 [1], 86 ± 6 [4] or 77.4 kJ/mol H_2 [3]. This reaction enthalpy is comparable to that of the more commonly known metal hydride, MgH_2 (74.06 kJ/mol H_2) [5], however, the advantage of Mg_2FeH_6 is its significantly high volumetric capacity 150 kg/m³ [6]. Properties such as excellent cyclability and high thermal stability also allows Mg_2FeH_6 to be a promising candidate for heat storage within concentrated solar plants [3,7–9] thus broadening its use as a practical material and highlighting the importance of material properties' characterisation.

Similarly, the deuteride, Mg_2FeD_6 is an important material to synthesise and study as it can be used to further investigate hydrogen interaction properties when studying isotopic exchange behaviour or neutron diffraction. One such study used neutron diffraction to analyse the absorption and desorption processes of Mg–Fe–H system and Mg_2FeD_6 was used to further understand these reaction mechanisms [10]. Mg_2FeH_6 has also been widely combined with other hydrides to improve hydrogen properties of the overall system especially with regards to thermodynamic stability [11–14]. Examples where Mg_2FeD_6 is used are the recent studies that Mg_2FeH_6 used in reactive hydride composite (RHC) systems together with light weight metal borohydrides namely Li-, Na-, Mg-, Ca- and K-borohydrides [12,15–17] have shown unique sorption behaviour different from the individual components. Chaudhary et al. [15] and Li et al. [16,17] both reported the appearance of single step desorption behaviour with these RHC at specific anionic stoichiometries with a suggestion of hydrogen exchange contributing to this phenomenon [18]. In order to observe this hydrogen exchange, Mg_2FeD_6 was synthesised and combined with the borohydride. The results showed evidence of H-D formation, either during ball milling or upon heating up to 400 °C, as H-D was released during the desorption process. In order to achieve such information, keeping the pressure low during raw material synthesis reduces the need for expensive compression systems and also minimises the quantity of gas necessary for use. This is especially the case when using high purity deuterium as it is much more expensive to purchase when compared to hydrogen gas.

To date, Mg_2FeH_6 and Mg_2FeD_6 (D_2 content 10.37 wt.%) are not produced commercially and are synthesised in individual laboratories [1,19–23]. Mg and Fe do not exist as an intermetallic compound but can be chemically bound in the form of Mg_2FeH_6 or Mg_2FeD_6 , thus posing some challenges to the synthesis method. The first reported synthesis of the compounds used elemental Mg and Fe sintered at 500 °C under hydrogen or deuterium pressures between 60 and 120 bar for up to 10 days [1]. However, there were significant amounts of MgH_2 or MgD_2 together with unreacted Mg and Fe remaining in the finished product. Subsequent studies have shown improved purity of Mg_2FeH_6 when Mg was first hydrogenated to MgH_2 before combining with Fe [3,19,21,24]. Since this was an effective method of increasing the reaction yield, this study has extended this idea with deuterium instead of hydrogen to

first synthesis MgD_2 before further reacting with Fe and D_2 to produce Mg_2FeD_6 . The literature also showed that reactive ball milling (milling in H_2 atmosphere) provided an improved synthesis route, however, evidence of MgH_2 , Fe and MgO was still present. High purity Mg_2FeH_6 synthesis was achieved more recently, by Polanski et al. [21] as the conditions used (500 °C and 120 bar H_2) were able to achieve a reaction yield of 94–97%. The work presented here limits the synthesis pressure of both reactive ball milling and direct annealing to 10 bar, the lowest pressure reported to date for, an order of magnitude lower than the high purity work shown in Polanski et al. [21]. In order to gain a high yield of product, various methods were used and compared including reactive milling in D_2 atmosphere and direct pressure to ascertain which method was best whilst keeping the pressure low to a maximum of 10 bar.

For some research institutes, in particular those in Japan, the use of any gas, including hydrogen and deuterium, is limited to 10 bar due to the High Pressure Gas Safety Act (Act No. 204 June 7, 1951). This poses some synthesis challenges. This work presented here addresses some of these challenges to provide a new high-yield production route for Mg_2FeD_6 under the given pressure limitations focussing on reactive planetary ball milling and the influence of synthesis parameters on the reaction yield.

Experimental methods

All materials for this work were handled in an argon atmosphere glovebox (Miwa, Japan) with a constant gas purifying system to reduce any risk of contamination from oxygen or water ($\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 1$ ppm).

In order to synthesise Mg_2FeD_6 , MgD_2 was first prepared from desorbed MgH_2 (Alfa Aesar, 98%), followed by deuterium D_2 (Asahi sunsoshokei, 99.99%) absorption at 10 bar. Table 1 gives the synthesis parameters used for the four batches of MgD_2 that were later used to prepare Mg_2FeD_6 . All batches of MgD_2 were prepared by loading as supplied or ball milled MgH_2 into a tube reactor where the material was heated to release H_2 and later low pressure D_2 was applied. Only batch 4

Table 1 – MgD_2 synthesis conditions.

Processing step	Batch 1	Batch 2	Batch 3	Batch 4
1st Step desorption				
Desorption temperature (°C)	400	450	450	450
Vacuum pressure (bar)	4×10^{-5}	4×10^{-5}	4×10^{-5}	4×10^{-5}
Desorption time (h)	1	4	2	4
Absorption temperature (°C)	360	360	400	400
Deuterium pressure (bar)	10	10	10	10
Absorption time (h)	2	12	4	4
2nd Step desorption				
Desorption temperature (°C)	400	–	–	–
Vacuum pressure (bar)	4×10^{-5}	–	–	–
Desorption time (h)	1	–	–	–
Absorption conditions				
Absorption temperature (°C)	360	–	360	360
Deuterium pressure (bar)	10	–	10	10
Absorption time (h)	10	–	6	6

Download English Version:

<https://daneshyari.com/en/article/5145745>

Download Persian Version:

<https://daneshyari.com/article/5145745>

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