Materials and Design 135 (2017) 239–245

Contents lists available at ScienceDirect

Materials and Design

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

Low temperature formation of Mg_2FeH_6 by hydrogenation of ball-milled nano-crystalline powder mixture of Mg and Fe

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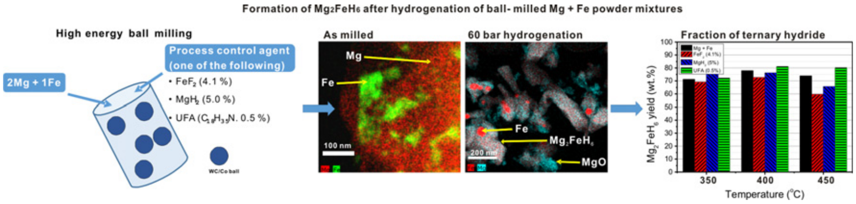
HIGHLIGHTS

- Mg_2FeH_6 was synthesized by hydrogenation of various Mg-Fe powder mixtures.
- A high yield of 81 wt% of Mg_2FeH_6 was obtained at 450 °C.
- A promising yield (>69 wt%) at 350 °C under 60 bars of H_2 was achieved.
- Cyclic experiments demonstrated the potential of the process for practical applications.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 July 2017
Received in revised form 15 September 2017
Accepted 16 September 2017
Available online 18 September 2017

Keywords:
Metal hydrides
Hydrogen solid-state storage
Thermal analysis
Transmission electron microscopy
Cycling ability

ABSTRACT

Low temperature formation of Mg_2FeH_6 is demonstrated by hydrogenation of Mg-Fe elemental powder mixture at a temperature as low as 350 °C which is lower than the conventional process temperature, 500 °C. To enable the low temperature synthesis, the powder mixture of Mg and Fe has been prepared by high energy ball milling using different process control agents (PCAs). A systematic study on the ball milling and hydrogenation conditions has been carried out to maximize the yield of the ternary line compound. The hydrogenation conditions together with the particle size of the starting materials turn out to play a significant role in the hydrogenation kinetics of the system. An optimized condition has demonstrated a significant hydrogenation as well as a robust cycling ability at low temperature which suggests the strong potential of the process for practical applications.

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1. Introduction

Hydrogen solid-state storage systems have been extensively investigated over the past decades in the light of their potential for sustainable energy sector development. Various metal hydrides were covered, from simulations [1] to practical storage experiments [2,3]. Among them, the MgH_2/Mg solid-state hydrogen storage system is well known for its superior storage capacity (7.6 wt% H_2), but it displays poor cycling properties: after few cycles the hydrogen storage capacity dramatically drops [4]. Such a degradation has been attributed to the poor stability of the microstructure during cycling at elevated temperatures. On the other hand, Mg-M-H complex hydrides (M: Co, Ni, and Fe) have been found to be highly promising in improving the cycling ability at the expense of the storage capacity. These complex hydride systems have shown large hydrogen storage capacities of 3.6 for Mg_2NiH_4, 4.4 for Mg_2CoH_5 and 5.5 wt% for Mg_2FeH_6 [5]. Although these values are smaller than that of the MgH_2/Mg binary system, they were proven to have a longer lifetime under cycling conditions [6,7].

Among the three late transition metals, the effect of Fe as a major additive to the basic Mg-H binary system is not to be questioned

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http://dx.doi.org/10.1016/j.matdes.2017.09.032
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considering the robust properties of the Mg-Fe-H system: competitive gravimetric H_2 density (5.5 wt% H_2), high heat storage density ($-77.4\ kJ\cdot mol^{-1}\ H_2$), high volumetric H_2 density ($150\ kg\cdot m^{-3}$) even higher than that of MgH_2 ($110\ kg\cdot m^{-3}$), and of course outstanding cycling ability (~1000 hydrogenation/dehydrogenation cycles) [6,8]. Although the Mg_2FeH_6 compound and its crystallographic structure have been reported in 1984 [9], its formation mechanism is still controversial. A two-step hydrogenation reaction is widely accepted: first the formation of MgH_2 during the exposure of Mg-Fe mixture to a hydrogen atmosphere, followed by the reaction of the newly formed MgH_2 with the remaining Fe and additional hydrogen [10–12]. This reaction pathway mainly results from the significant difference in the formation kinetics between MgH_2 and Mg_2FeH_6: MgH_2 always forms first [10–12]. This two-step synthesis route has been systematically observed, while the one-step reaction, a direct hydrogenation of Mg and Fe into Mg_2FeH_6, has not. Nevertheless, the one-step pathway is yet theoretically possible as long as the pressure-temperature conditions are selected to be below the decomposition pressure of MgH_2 [6,9,13,14]. In this case, MgH_2 is thermodynamically not stable and therefore cannot form; thermodynamics is in favor of a direct synthesis of the ternary hydride, Mg_2FeH_6.

The dehydrogenation process on the other hand has been found to be a one-step reaction, during which the ternary hydride decomposes into the two distinct mutually-immiscible Mg and Fe phases. This phase separation is thought to be the major source of the remarkable cycling properties considering that the decomposed Fe phase would prevent agglomeration and growth of Mg particles which is responsible for the capacity drop upon cycling [6,8]. In other words, the decomposition of Mg_2FeH_6 takes place in nanometer scale regardless of the initial particle or grain size of the ternary hydride, therefore maintaining the refined microstructure throughout the cycling.

Despite the benefits of Mg_2FeH_6, no practical method to synthesize the ternary hydride with sufficient level of quality as well as quantity for commercial application has been developed yet. Only high temperature synthesis for the heat storage application for which the working temperature ranges around 500 °C was reported [6,8]. For the application as a solid state hydrogen storage medium, limiting the operation temperature for both initial synthesis and cyclic service below certain level to guarantee the energy efficiency is desirable. In this regard, it has been of the highest interest to synthesize Mg_2FeH_6 in an efficient way from the separately given Mg and Fe metals at lower temperature than the one reported for heat storage application.

The synthesis of Mg_2FeH_6 in laboratory scale is widely documented and synthesis routes are numerous. For example, there are different methods even in ball milling process: (i) ball-milling followed by hydrogenation [15,16] (also for other complex hydrides such as the Mg-Co-H system [17]), or (ii) reactive ball-milling (in hydrogen atmosphere) [10, 18–21], or even (iii) cryo-milling [13]. In addition, the choice of the starting materials has been demonstrated to be critical in the synthesis results [20,22]. Among the different combinations, the procedure utilizing high energy ball milling followed by hydrogenation of a mixture of commercially available metal powder, Mg and Fe, appears the most promising for practical applications. Properly designing the fabrication procedure as well as the microstructural features of the resulting materials is therefore a key and major aspect that has to be considered in order to achieve the aforementioned large scale applicability.

This study thus focuses on improving the processing technique, by introducing process control agents (PCAs) in Mg and Fe powder mixtures with the aim of manufacturing a fine and homogeneous nanocomposite via high energy ball-milling. The hydrogenation properties of the ball-milled materials were investigated, with the purpose of evidencing their faster and more efficient hydrogen absorption capacity at lower process temperature than the reported ones. Ultimately, our goal was to improve the fabrication process by proposing a method that enables a fine tuning and design of the structure of the metallic composite at nanometer-scale. In addition, we intended to demonstrate the feasibility, reproducibility and reliability of the suggested procedure, as well as to demonstrate its practicability for larger scale applications.

2. Experimental details

Elemental Mg powder (Alfa Aesar, 99.8%) and Fe powder (Sigma Aldrich, ≥99.5%) were mechanically ball-milled for 1 h in Ar atmosphere, using the SPEX-8000 (Nano force, 8000 M Mixer/Mill (Mono type), 1,402,897,832) ball milling apparatus. Prior to milling, the Mg-Fe mixture (2:1 M ratio) and 15 WC/Co balls with a diameter of 10 mm were loaded in the milling cylinder. The ball to powder weight ratio was 40:1. Except for the cases of using Unsaturated Fatty Amine ($C_{18}H_{35}NH_2$) as a PCA which will be explained in detail in the following Section 3.1, the samples were prepared in an Ar glove box ($p(CO_2,O_2) <$ 0.1 ppm) in the purpose of preventing any contact with air. The milling process was interrupted every 15 min in order to rotate the milling container at 90 degrees and flip it backwards. This manipulation was repeated four times in total to prevent the milling energy from concentrating on a single side of the milling cylinder. The produced material was stored in the glove box after processing.

The hydrogenation experiment was carried out via three different approaches: high temperature single step hydrogenation (24 h, 450 °C, 35 and 60 bars of hydrogen), lower temperature single step hydrogenation (24 h, 350 and 400 °C, 60 bars of hydrogen) to observe the temperature dependence of the hydrogenation, and finally multistep cyclic hydrogenation (~5 cycles of hydrogenation and dehydrogenation, 60 bars for 2 h and 5 bars for 2 h at the fixed temperature of 400 °C for hydrogenation and dehydrogenation, respectively). Hydrogen charging was conducted using a Sievert-type apparatus equipped with high and low pressure gages. Once the hydrogen charging completed, the specimen chamber was abruptly cooled down by dipping into a quenching bath of ice water.

The synthesized materials were characterized by means of various analysis tools such as Pressurized Differential Scanning Calorimetry (PDSC, DSC-204 HP Phoenix, NETZSCH) to investigate the thermal properties, X-ray Diffraction (XRD, Bruker D8 Advance X-ray Diffractometer System) and Transmission Electron Microscopy (TEM, Talos F200X, FEI) to observe and characterize the microstructure both before and after hydrogenation. The yield (in wt%) as well as the size of crystals (in nm) of each phase composing the studied systems were computed via TOPAS software using the Rietveld's refinement method.

3. Results and discussions

3.1. The starting material

Several mixtures of Mg and Fe (2:1 M ratio) were ball-milled together with various amounts and compositions of process control agents (PCAs). Thus, MgH_2 (2.5, 5, 7.5, and 10 wt%), FeF_2 (1.1, 2.1, 3.1 and 4.1 wt%), FeF_3 (5 and 10 wt%), and Unsaturated Fatty Amine ($C_{18}H_{35}NH_2$), later on referred to as UFA (0.2 and 0.5 wt%) were utilized as PCAs. They were purposely selected with regards to the following aspects: (i) by the addition of MgH_2, facilitating the milling process by introducing ductile-brittle interactions to the initially ductile-ductile Mg-Fe mixture [10], therefore leading to a particle size reduction which is beneficial to the hydrogen storage capacity [23–25]; (ii) by the addition of FeF_2 (or FeF_3), achieving faster hydrogen absorption kinetics through the modification of Mg surface properties [26,27], and forming a surface protective layer [28] both via MgF_2 formation; and (iii) by the addition of UFA whose effect on the Mg-Fe-H system has not been reported yet, investigating the hydrogenation capability of ball-milled powder mixtures produced using this commercially available organic PCA. The selected powder mixtures were prepared accordingly to the procedure described in the ‘experimental details’ section.

The high energy ball-milling process produced a crystalline structure composed of Fe and Mg, irrespective of the composition of the powder

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