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Synthesis of Mg_2FeH_6 by hydrogenation of Mg/Fe powder mixture prepared by cold roll milling in air: Effects of microstructure and oxygen distribution

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ABSTRACT

Herein, we describe the synthesis of Mg_2FeH_6 by hydrogenation of a 2.1 Mg/Fe (mol/mol) powder mixture prepared by cold roll milling (CRM) in air. The thickness of Fe layers and the amount and distribution of oxygen with number of CRM passes were systematically analyzed. CRM-induced microstructural changes were shown to play an important role in Mg_2FeH_6 formation. Although repeated CRM effectively decreased the Fe layer thickness to values sufficient for the fast formation of Mg_2FeH_6 , too much CRM passes decreased the total degree of hydrogenation due to inevitable oxidation of Mg in air. Both microstructure refinement and minimal oxidation are the prerequisites for efficient Mg_2FeH_6 synthesis, with the former condition being achievable by optimizing the number of milling passes, and the latter one requiring CRM under an inert atmosphere.

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Introduction

Among numerous solid-state hydrogen storage materials, Mg-based metal hydrides such as MgH_2 [1–6], Mg_2FeH_6 [6–17], Mg_2NiH_4 [18–20], and Mg_2CoH_5 [9,21,22] have attracted much

attention. Particularly, MgH_2 and Mg_2FeH_6 are attractive because of their high hydrogen storage capacity and low raw material costs [23–25]. Specifically, MgH_2 has a high gravimetric density of 7.6 wt%, whereas the corresponding volumetric density ($110 \text{ kgH}_2/\text{m}^3$) is low compared to AB_5 - (about

Abbreviations: Cold roll milling, CRM; oleylamine, OA; high pressure differential scanning calorimetry, HP-DSC; scanning electron microscopy, SEM; transmission electron microscopy, TEM; thermogravimetric analysis, TGA; X-ray diffraction, XRD; energy-dispersive X-ray spectroscopy, EDS.

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125 kgH₂/m³) and AB₂-type (about 130 kgH₂/m³) hydrogen storage alloys [26]. Although its gravimetric density of 5.5 wt% is lower than that of MgH₂, Mg₂FeH₆ exhibits the highest volumetric density among the known metal hydrides (150 kgH₂/m³), additionally featuring excellent reversibility (over 500 cycles above 450 °C and hydrogen pressures below 100 bar). These excellent hydrogen storage properties make Mg₂FeH₆ a promising component of stationary hydrogen storage systems, allowing high temperature thermal storage units to be implemented using compact storage tanks [2,16,27].

High energy [28–31] and reactive ball milling [32–36] are the most commonly used methods for synthesizing Mg-based hydrogen storage materials, being accompanied by subsequent high temperature sintering under hydrogen pressure [9,10,25,28,30]. Another method is high pressure synthesis of the mixed powder [19,37]. In general, ball milling improves the hydrogenation rate due to producing nanocrystalline powders and decreasing the diffusion distances among the constituents. Recently, cold roll milling has been adopted to improve the rate of MgH₂ synthesis, affording nanocrystalline powders and being superior to ball milling in terms of time, cost, and energy efficiency [38–43]. In addition, cold roll milling is well suited for continuous mass production, irrespective of whether it is performed in an inert or ambient atmosphere. To date, only several studies on the roll milling of Mg [40,43] or MgH₂ [38,39,41] have been conducted, and even less is known about the roll milling of Mg and Fe to produce Mg₂FeH₆ [29,42]. However, these studies [29,42] utilize additional high energy ball milling or extrusion process before applying the cold roll milling process.

The CRM optimization strategy can be devised based on the mechanism of Mg₂FeH₆ formation, with two plausible pathways suggested, namely (i) direct formation of Mg₂FeH₆ (2 Mg + Fe + 3H₂ = Mg₂FeH₆ [16,30,44,45]) and (ii) initial formation of MgH₂ and its subsequent reaction with Fe in the presence of excess H₂ to form Mg₂FeH₆ [7,13,46,47]. However, we believe that the method of synthesizing Mg₂FeH₆ by reactive ball milling [7,13,46] is inevitably in favor of the second mechanism because Mg can quickly react with hydrogen to form MgH₂ before both Mg and Fe become fine enough to react simultaneously with hydrogen to form Mg₂FeH₆ directly. On the other hand, when homogeneous mixture of Mg and Fe nanoparticles is pressed into a compact and then hydrogenated at 400 °C under 40 bars [47], they observed that MgH₂ forms first before the formation of Mg₂FeH₆.

In the second mechanism, which is known to be more efficient, the continuous formation of Mg₂FeH₆ is supported by the diffusion of external MgH₂ through the layer of previously formed Mg₂FeH₆ and the reaction of MgH₂ with internal Fe. It is believed that the diffusion rate of MgH₂ (or Mg) through the Mg₂FeH₆ layer is much faster than that of Fe. As the Mg₂FeH₆ layer becomes thicker, the increased time required for external MgH₂ diffusion hinders the formation of Mg₂FeH₆, resulting in significant amounts of unreacted Fe and MgH₂ [7]. Hence, the fast formation of Mg₂FeH₆ relies on the reduction of Mg or MgH₂ diffusion distances by decreasing the size of Fe particles, which becomes more critical under the conditions of low reaction temperature (i.e., 400 °C in this study) and slow diffusion.

The size of Fe particles (or Fe layer thickness) was controlled by varying the number of CRM passes to correlate it with the degree of Mg₂FeH₆ formation. Moreover, the CRM process was further simplified by being performed in ambient atmosphere. Due to the unavoidability of oxidation under these conditions, we also investigated the evolution of oxide distribution and content as a function of CRM pass number. To summarize, we herein highlight two important aspects of Mg₂FeH₆ synthesis by CRM in air, namely (i) the effect of diffusion distance, i.e., thickness of Fe layers controlled by the number of CRM passes, and (ii) the effect of MgO formation during CRM.

We herein describe the use of simple cold roll milling (CRM) which may be one of the most efficient methods of synthesizing Mg₂FeH₆. As reported, the higher the contact surface between Mg and Fe, the higher the yield and the shorter the synthesis time [12]. We used powders instead of plates to maximize the contact area between Mg and Fe and to easily collect the powder under the rolls. After CRM, Mg₂FeH₆ was synthesized by hydrogenation at 400 °C, as the yield of Mg₂FeH₆ was previously reported to be higher at lower temperature (400 °C) than at higher temperature (450 °C) [48].

Experimental

Mg (>98.5%, 75–250 μm) and reduced Fe (>99%, 38–150 μm) powders were pre-mixed in ambient atmosphere in a molar ratio of 2.1:1, and 0.5 wt% of oleylamine (OA) was added. The extra 0.1 mol of Mg was added due to the high reactivity of this metal leading to its oxidation and thus increasing consumption during processing. OA was utilized as a process control agent to prevent the agglomeration of powders and their sticking to the rolls during milling. In addition, OA had a beneficial effect on the roll milling process and subsequent hydrogenation, improving the yield of the ternary hydride [48]. The pre-mixed powders were milled using an in-house-made vertical roll milling machine for up to 50 passes in steps of 10 passes at 50 rpm in ambient atmosphere. Specifically, one pass was defined as the moment when all powder in the powder feeder had passed through the roll. The milling machine comprised two vertical rolls (diameter = 100 mm), a vibrational powder feeder capable of regulating the amount and speed of the powder input, and an inlet for stable spill-free powder entry between the rolls.

For hydrogen charging, samples prepared in ambient atmosphere were loaded into a Sievert-type device equipped with low and high pressure gauges. Subsequently, the chamber was evacuated, immediately charged with 60 bar of hydrogen (without argon purging), and heated to 400 °C for 6 h. Finally, the temperature was lowered by soaking the sample holder in ice water for 30 min, and the hydrogenated samples were collected and stored in an Ar-filled glove box (*p* (H₂O, O₂) < 0.1 ppm). Table 1 summarizes the notation employed for specimens prepared under different conditions.

Thermal properties and hydrogenation kinetics were investigated by high pressure differential scanning calorimetry (HP-DSC; DSC-204 HP Phoenix, NETZSCH) and thermogravimetric analysis (TGA; TG-209 F1, NETZSCH). HP-DSC analysis performed at a heating rate of 10 °C/min under

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