Direct mechanical synthesis and characterisation of $Mg_2Fe(Cu)H_6$

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Abstract

Direct synthesis of Mg_2FeH_6 was carried out by mechanically alloying MgH_2 with Fe under both Ar and H_2 atmospheres. Both $(3MgH_2+Fe)$ and $(4MgH_2+Fe)$ mixtures were processed to improve the yield of Mg_2FeH_6. The $(MgH_2–Fe–Cu)$ system was also investigated to modify the properties of the synthesised compound. X-ray diffraction and Rietveld analysis were carried out to determine the phase evolution of the powder mixtures. Field emission SEM clearly showed substantial particle size reduction for the mixture milled under hydrogen. Thermogravimetry (TG) was employed to determine the dehydrogenation kinetics of the milled mixtures.
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Keywords: Hydrogen storage materials; Mechanical alloying; Mg-based alloy; Mg_2FeH_6

1. Introduction

Mg and Mg-based alloys are a group of attractive materials for hydrogen storage applications. MgH_2 provides a high storage capacity of 7.6 wt% hydrogen. Many research efforts have been devoted to modifying the Mg–H system in order to achieve rapid hydrogenation/dehydrogenation kinetics, cyclic stability and low desorption temperature.

It is well known that the ternary hydride compound, Mg_2FeH_6, shows a high hydrogen-storage capacity of 5.5 wt%, it is desirable for hydrogen storage. However Mg_2FeH_6 is more difficult to synthesize than the conventional transition metal hydride, Mg_2NiH_4. In the past, Didisheim et al. [1] showed that Mg_2FeH_6 could be synthesized by sintering the cylindrical pellets of Mg and Fe powders mixed in a 2:1 atomic ratio at around 500 °C under 20–120 bar of H_2 pressure. More recently, Huot et al. [2] firstly reported a high yield of 65 wt% Mg_2FeH_6 by milling the mixture of $(2Mg+Fe)$ in a planetary ball mill under H_2 atmosphere for 20 h, followed by sintering at 623 K under 50 bar of H_2. Thereafter, Huot et al. [3] synthesised the hydride by direct milling of the stoichio-

metric $(2MgH_2+Fe)$ under Ar atmosphere up to 60 h, leading to a yield of 56 wt% of Mg_2FeH_6. Gennari et al. [4] reported that mechanically alloying the mixture of $(2Mg+Fe)$ in 5 bar of H_2 atmosphere led to the formation of Mg_2FeH_6. However, the yield after 60 h of milling was only 30 wt%. Sai Raman et al. [5] improved the conditions used in Ref. [4], and achieved 63 wt% Mg_2FeH_6 under a H_2 pressure of ~10 bar after only 20 h of high-energy milling. So far this is the highest amount of Mg_2FeH_6 produced via a single process of mechanical alloying.

However, the previous studies on the synthesis of Mg_2FeH_6 often involve the stoichiometric composition of $(2MgH_2/Mg+Fe)$ and an unexpectedly large amount of un-reacted species, e.g. Mg, Fe and/or MgH_2, still existed in the final mixture. Moreover, the sorption kinetics of the Mg–Fe–H system has not been reported so far.

In this study, direct synthesis of Mg_2FeH_6 by mechanically alloying MgH_2 with Fe under both Ar and H_2 atmospheres were investigated in order to optimise the conditions of forming Mg_2FeH_6. Both $(3MgH_2+Fe)$ and $(4MgH_2+Fe)$ mixtures were selected with the aim of improving the yield of Mg_2FeH_6, while reducing the level of un-reacted species. Furthermore, the $(MgH_2–Fe–Cu)$ system was also studied with an attempt to modify the hydrogen storage properties of the Mg_2FeH_6 and stabilize the Mg_2Fe binary compounds in air before hydriding. The hydrogen desorption properties of the final mixtures were studied using simultaneous thermogravimetry and differential scanning calorimetry (TG/DSC).

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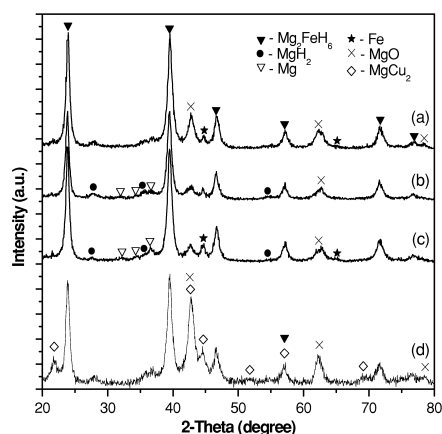
Fig. 1. XRD patterns of 60-h milled mixtures: (a) $(4MgH_2 + Fe)$ under H_2; (b) $(4MgH_2 + Fe)$ under Ar; (c) $(3MgH_2 + Fe)$ under Ar; and (d) $(3MgH_2 + 0.5Fe + 0.5Cu)$ under Ar.

2. Experimental methods

The starting materials were Mg hydride powder ($95\%MgH_2$, $5\%Mg$, 6 μm) from Th. Goldschmidt, and Fe (99.8%, 7 μm) and Cu (99.9%, 149 μm) powders from Strem Chemical. The powders were weighed and mixed within an Ar-filled glove box. Milling was carried out using a Fritsh P5 planetary ball mill under H_2 or Ar atmosphere. For each experiment, about 6 g of powder and six stainless-steel balls of 20 mm in diameter were used, leading to a ball-to-powder weight ratio of about 30. A relatively common milling speed of 250 rpm was selected. The vial was evacuated first and filled with H_2 or Ar before each operation. A small amount of powder was taken at regular intervals for analyses. For the (MgH_2–Fe–Cu) system, MgH_2 was milled with Fe and Cu under Ar atmosphere with the composition of ($MgH_2 + 12.5$ mol%Fe + 12.5 mol%Cu), hereafter, termed as ($3MgH_2 + 0.5Fe + 0.5Cu$). The ball-to-powder weight ratio and milling speed were the same as the ($MgH_2 + Fe$) mixture. Milling was carried out up to 60 h. The X-ray diffraction characterisation was performed using a D5000 Siemens diffractometer with Cu Kα radiation. Qualitative and quantitative Rietveld analyses were carried out using the Rietan programme [6]. A Jeol 6300 Field Emission Scanning Electron Microscope was employed to characterise the particle size and surface morphologies of the powder

mixtures. Hydrogen desorption kinetics and thermal behaviour of the prepared samples were studied using a Setaram Setsys16/18 TG/DSC system with a precision of 0.1 μg during heating under a hydrogen partial pressure.

3. Results and discussion

3.1. X-ray diffraction patterns

Fig. 1 shows the X-ray diffraction patterns of the milled powders. The formation of the Mg_2FeH_6 phase is noted with the existence of additional diffraction peaks, which may be attributed to the orthorhombic high-pressure metastable γ-MgH_2 phase. A very small amount of MgH_2 and Fe was also detected. The possible reaction during milling, leading to the formation of Mg_2FeH_6, is:

$$3MgH_2 + Fe \rightarrow Mg_2FeH_6 + Mg \quad (1)$$

From reaction (1), all the MgH_2 should be consumed during the formation of Mg_2FeH_6 in the mixture of ($3MgH_2 + Fe$) with some level of Mg. The latter was in fact oxidized into MgO by oxygen residual in the atmosphere, due to the high reactivity of fine Mg particles. For the ($3MgH_2 + 0.5Fe + 0.5Cu$) mixture, it is noted that an $MgCu_2$ phase was formed during milling.

3.2. Rietveld analysis

Rietveld analysis was carried out to determine the evolution of phase composition and phase abundance of the milled mixtures and the results are reported in Table 1. It is noted that the level of Mg_2FeH_6 was 80, 71, 62 and 40 wt%, respectively, for the ($3MgH_2 + Fe$) milled under Ar, the ($4MgH_2 + Fe$) milled under Ar, the ($4MgH_2 + Fe$) milled under H_2, and the ($3MgH_2 + 0.5Fe + 0.5Cu$) milled under Ar. The lowest yield was obtained when adding Cu to the ($MgH_2 + Fe$) mixture, which is mainly due to the formation of the $MgCu_2$ phase and the following possible reaction:
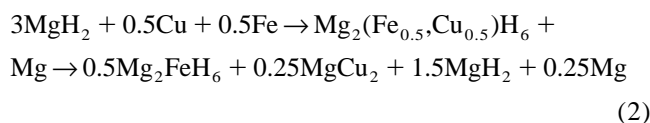
$$3MgH_2 + 0.5Cu + 0.5Fe \rightarrow Mg_2(Fe_{0.5},Cu_{0.5})H_6 +$$

$$Mg \rightarrow 0.5Mg_2FeH_6 + 0.25MgCu_2 + 1.5MgH_2 + 0.25Mg$$

$$(2)$$

Table 1
Rietveld refinement of the X-ray diffraction patterns of the mixtures of ($3MgH_2 + Fe$), ($4MgH_2 + Fe$) and ($3MgH_2 + 0.5Fe + 0.5Cu$), milled for 60 h

Phase (wt%)	$3MgH_2 + Fe$ (under Ar)	$4MgH_2 + Fe$ (under Ar)	$4MgH_2 + Fe$ (under H_2)	$3MgH_2 + 0.5Fe + 0.5Cu$ (under Ar)
'S'[a]	1.46	1.31	1.26	1.12
Mg_2FeH_6	79.46	70.94	61.87	40.14
Fe	4.10	1.99	1.42	–
MgO	16.44	19.35	32.93	35.61
MgH_2	–	7.71	3.78	2.34
$MgCu_2$				21.91

[a] Goodness-of-fit.

Moreover, a large amount of MgO has been formed during milling, reaching 35 wt% in the $(3MgH_2 + 0.5Fe + 0.5Cu)$ mixture. During the formation of the Mg_2FeH_6 phase, the free Mg reacted readily with oxygen to produce MgO.

3.3. Microstructural characterization: SEM analysis

An SEM image of the $(4MgH_2 + Fe)$ mixture milled under argon, Fig. 2c, shows very fine particles. The particles are even smaller when milled under H_2 atmosphere, as seen in Fig. 2d. H_2 can reduce the cold welding and agglomeration of the particles. Fig. 2e shows an image at a high magnification for the mixture milled under hydrogen, where agglomeration of nano-particles is seen on the surface of the large particles.

SEM image of the milled $(3MgH_2 + 0.5Fe + 0.5Cu)$ mixture, Fig. 2f, shows inhomogeneous particle size distribution, where large particles are dispersed among fine particles.

3.4. Thermogravimetric analysis

The hydrogen desorption was carried out under 0.1 bar H_2 pressure. The hydrogen desorption curves of the $(3MgH_2 + Fe)$ and $(4MgH_2 + Fe)$ mixtures at 320 °C are shown in Fig. 3. The $(3MgH_2 + Fe)$ mixture exhibits faster desorption kinetics by completely releasing hydrogen (3.6 wt%) within 1000s, whereas the $(4MgH_2 + Fe)$ mixture milled under Ar and H_2 shows slower kinetics with only about 3.0 and 2.2 wt%H_2 release, respectively. The $(4MgH_2 + Fe)$ mixture milled under H_2 shows the slowest hydrogen desorption kinetics at 320 °C. This may be due to
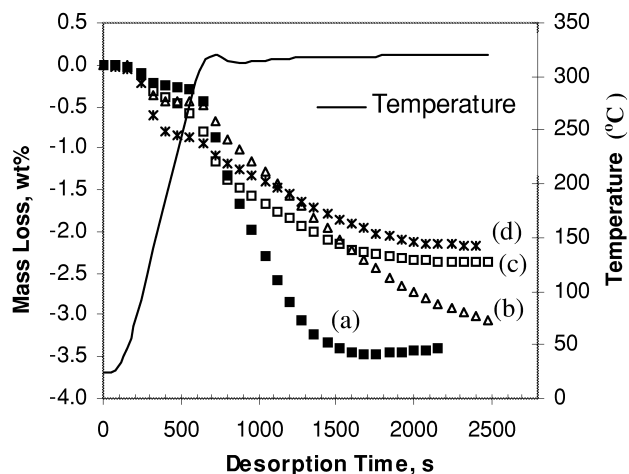

Fig. 3. Hydrogen desorption curves at 320 °C: (a) $(3MgH_2 + Fe)$ under Ar; (b) $(4MgH_2 + Fe)$ under Ar; (c) $(3MgH_2 + 0.5Fe + 0.5Cu)$ under Ar; and (d) $(4MgH_2 + Fe)$ under H_2. All mixtures were milled for 60 h.

the formation of a high level of MgO on the surface of the hydride particles, which hinders hydrogen desorption.

The $(3MgH_2 + 0.5Fe + 0.5Cu)$ mixture releases about 2.25 wt%H_2 at 320 °C and the kinetics is similar to the $(4MgH_2 + Fe)$ milled under H_2. Therefore, the substitution of 12.5 mol% Fe by 12.5 mol% Cu does not give rise to any improvement of the dehydrogenation properties.

4. Conclusions

Mg_2FeH_6 hydride has been successfully synthesised by mixing MgH_2 and Fe, with a high yield of about 80 wt% using a ratio of MgH_2:Fe = 3:1. Increasing the MgH_2:Fe
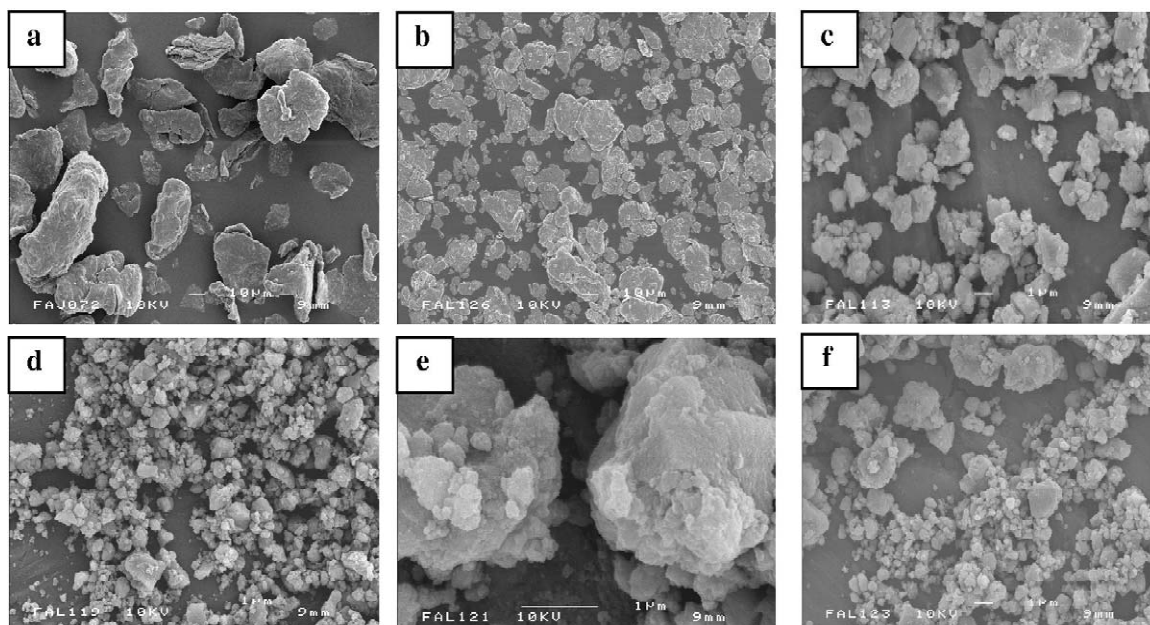

Fig. 2. SEM images: (a) as-received MgH_2; (b) as-received Fe; (c) $(4MgH_2 + Fe)$ milled under Ar for 60 h; (d) $(4MgH_2 + Fe)$ milled under H_2 for 60 h; (e) $(4MgH_2 + Fe)$ milled under H_2 for 60 h at a high magnification; and (f) $(3MgH_2 + 0.5Fe + 0.5Cu)$ milled under Ar for 60 h.

ratio to 4:1 did not improve the yield. The substitution of 50% of Fe by Cu, leads to the formation of $MgCu_2$, which reduces the final yield of Mg_2FeH_6 phase to 40 wt%. The dehydrogenation process carried out at 320 °C under 0.1 bar of H_2 pressure shows relatively fast dehydrogenation kinetics of the $(3MgH_2 + Fe)$ mixture milled under argon atmosphere.

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