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Ball-milling and AlB_2 addition effects on the hydrogen sorption properties of the $CaH_2 + MgB_2$ system

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ABSTRACT

Among the borohydrides proposed for solid state hydrogen storage, $Ca(BH_4)_2$ is particularly interesting because of its favourable thermodynamics and relatively cheap price. Composite systems, where other species are present in addition to the borohydride, show some advantages in hydrogen sorption properties with respect to the borohydrides alone, despite a reduction of the theoretical storage capacity. We have investigated the milling time influence on the sorption properties of the $CaH_2 + MgB_2$ system from which $Ca(BH_4)_2$ and MgH_2 can be synthesized by hydrogen absorption process. Manometric and calorimetric measurements showed better kinetics for long time milled samples. We found that the total substitution of MgB_2 with AlB_2 in the starting material can improve the sorption properties significantly, while the co-existence of both magnesium and aluminum borides in the starting mixture did not cause any improvement. Rietveld refinements of the X-ray powder diffraction spectra were used to confirm the hypothesized reactions.

1. Introduction

Complex hydrides (above all alanates, amides, and borohydrides) [1] have been intensively studied in recent years because of their higher theoretical hydrogen storage capacity if compared to traditional transition metals hydrides. Calcium borohydride, in particular, has been shown to release about 9.0 wt% of hydrogen if heated up to 550 °C [2]. MgH_2, which releases more than 7 wt% of hydrogen at 300 °C, is the most studied metal hydride and is being investigated for possible practical applications [3–5]. In this framework we decided to focus on the promising $Ca(BH_4)_2 + MgH_2$ reactive hydride composite (RHC) [6–8]. We studied the influence of milling time on the formation of the hydrogenated system from calcium hydride and magnesium boride. In addition, we investigated the effect of the addition of aluminum boride on the kinetic and thermodynamic hydrogen sorption properties.

2. Materials and methods

The starting materials calcium hydride (98%, −10 mesh) and magnesium diboride (−100 mesh) were purchased from Alfa Aesar, while aluminum diboride (≥96%, −325 mesh) was bought from Sigma–Aldrich. The samples were ball milled in a Spex8000M Mixer/Mill for different milling times (from 2 min to 900 min), performing 15 min milling followed by 15 min pause steps to avoid sample heating inside the hardened steel milling vial. All the powders have been handled inside an Ar filled glove box (MBraun) with moisture and oxygen level kept below 1 ppm. Amounts of powder ranging from 0.45 g to 0.65 g were introduced in an automatic manometric Sievert's type gas reaction analyzer, PCTPro-2000 by Setaram. Concerning the absorption tests, the samples were charged with an initial pressure of 120 bar, then a temperature ramp from room temperature to 360 °C was performed at 5 °C/min rate, followed by an isothermal step (lasting 1400 min or 3000 min) at 360 °C. Isothermal dehydrogenation runs were performed on the absorbed samples at 390 °C under static vacuum. Coupled manometric–calorimetric measurements were performed by coupling the manometric instrument with the Sensys DSC instrument (Setaram). 50 mg of the samples hydrogenated in the manometric apparatus were loaded in the high pressure cell of the Sensys apparatus under Ar atmosphere inside the glove box. The cell was inserted in the furnace of the DSC instrument and connected with the manometric instrument by a 1/8′ stainless steel tube. The powders were subjected to a thermal programmed desorption (TPD) measurement performed by heating from room temperature to 580 °C at 2 °C/min with a starting hydrogen pressure of 0.1 bar. The integration of the calorimetric peaks was made by Calisto software (Setaram). X-ray powder diffraction (XRPD) measurements have been performed using a Bruker D8 Advance diffractometer with Bragg–Brentano geometry and Cu Kα radiation. Rietveld refinements on the XRPD profiles have been performed using the software MAUD [9].

3. Results and discussions

3.1. Effect of milling time on $CaH_2 + MgB_2$ samples

Calcium borohydride and magnesium hydride can be obtained from calcium hydride and magnesium boride [8], according to the

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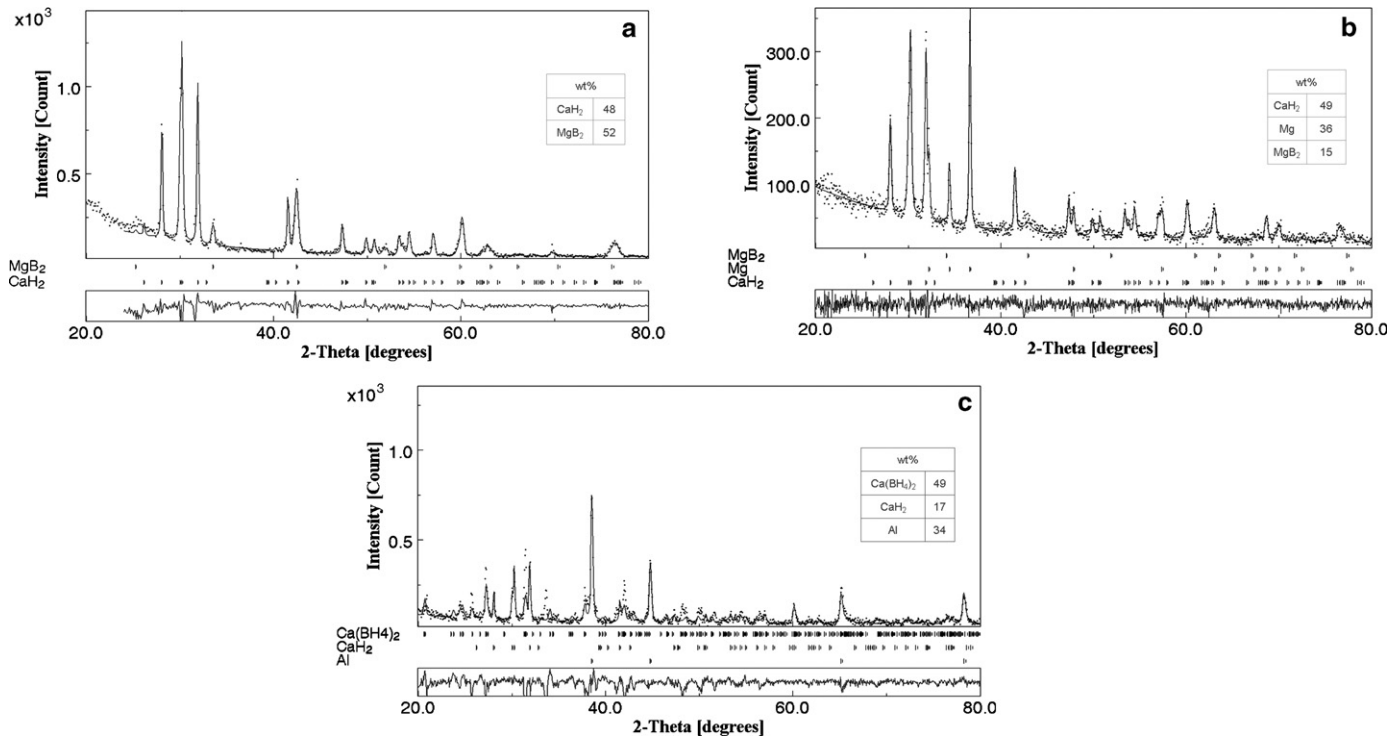

Fig. 1. XRPD patterns for different samples: (a) $CaH_2 + MgB_2$ after milling for 90 min; (b) $CaH_2 + MgB_2$ milled for 90 min, hydrogenated and subsequently desorbed; (c) $CaH_2 + AlB_2$ milled for 90 min and hydrogenated. The insets show calculated weight content of the constituent phases.

reaction:

$$CaH_2 + MgB_2 + 4H_2 \rightarrow Ca(BH_4)_2 + MgH_2 \quad \text{theoretical } H_2 \text{ content} = 8.39\,\text{wt\%} \qquad (1)$$

Four samples of calcium hydride and magnesium boride were prepared by milling for 2, 90, 450 and 900 min, respectively. As shown in Fig. 1(a), milling does not lead to the formation of any new phase, but decreases the crystallites size of the starting hydrides (see Table 1). In Fig. 2 we compare the effect of milling time on the hydrogenation kinetics, and one can observe improved kinetics for the longer time milled samples. It is worth noting that the sample milled for 450 min shows the best kinetics just at the beginning, getting worse with respect to the 900 min milled sample after 0.5 h. XRPD analysis performed on the 90 min milled $CaH_2 + MgB_2$ sample after hydrogenation revealed a strong presence of the intermediate phase $Ca_4Mg_3H_{14}$ [8], together with the desired borohydride, magnesium hydride and some unreacted MgB_2 (Fig. 3), thus indicating that full absorption did not occur.

Fig. 4 shows the absorption and the desorption curves recorded for the 90 min milled sample, which takes 3600 min to reach

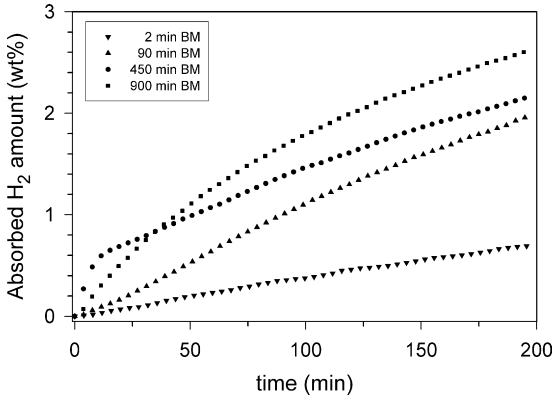

Fig. 2. Effect of milling time on the absorption kinetics (first 200 min) for $CaH_2 + MgB_2$ milled samples. Absorption was performed at 360 °C and starting hydrogen pressure = 120 bar. The crystallite size reduction improves the hydrogenation kinetics as milling time increases. The 450 min milled sample shows the fastest kinetics in the initial part of the charging procedure.

Table 1
Results obtained by XRPD, manometric and coupled manometric-calorimetric measurements on $CaH_2 + MgB_2$ milled samples. Milling time has a clear effect on powder size, hydrogen capacity and release onset temperature. Crystallites size (with estimation error of 5%) for CaH_2 and MgB_2 have been obtained as a result of Rietveld analysis performed on the patterns by the software MAUD [9].

Sample	Crystallites size for the as milled samples (Å)		H_2 desorbed amount after hydrogenation for 1400 min (wt%)	Hydrogen release onset (°C)	ΔH double-peak (kJ/mol H_2)
	CaH_2	MgB_2			
($CaH_2 + MgB_2$) as milled for 2 min	1260	880	3.2	348	49.0
($CaH_2 + MgB_2$) as milled for 90 min	230	360	4.6	346	49.7
($CaH_2 + MgB_2$) as milled for 450 min	160	280	4.9	338	49.5
($CaH_2 + MgB_2$) as milled for 900 min	–	–	5.8	336	50.7