Hydrogen storage properties of MgH$_2$-diatomite composites obtained by high-energy ball milling

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Summary

To investigate the effects of specific porous microstructure of diatomite on the hydrogen storage properties of MgH$_2$, a two-step preparation was carried out. The first step was decrepitation of MgH$_2$ particle size during 10 h of milling. The second step was additional 1 h of milling with diatomite. The microstructure and phase composition of materials was characterized by X-ray diffraction, whereas the powder morphology and degree of additive dispersion were analyzed by scanning electron microscopy. The hydrogen desorption behaviour of nanocomposites was investigated by differential scanning calorimetry. The results show that addition of porous diatomite structure leads to decrease in desorption temperature, since there was no other effect that can have an influence on kinetics, such as formation of the metastable γ-phase, reduction of oxides to the native metal and/or homogeneous dispersion of the catalyst. This indicates that the microstructure of added material plays the main role in the enhancement of desorption properties of composites.

Introduction

Magnesium hydride (MgH$_2$) is an attractive energy storage material owing to its high storage capacity by weight (7.6 wt%), low weight and high volumetric density (Schlapbach & Züttel, 2001). However, its high dissociation temperature, slow hydriding–dehydriding kinetics and its reactivity to oxidation limit its use for hydrogen-related applications. The most widespread approach for improving its reaction kinetics is mechanical milling with additives through two effects: one is assisting nucleation by creating many defects on the surface and/or in the interior of MgH$_2$ and

the other is shortening of diffusion distances by reducing the effective particle size. Both effects result in growth in the specific surface area (Song, 1995). Recently, it was shown that mixing oxides with magnesium and using mechanical milling allow improvement of the sorption properties (Oelerich *et al.* 2001; Song *et al.*, 2005; Barkhodarian *et al.*, 2004; Sub Lee *et al.*, 2004). Furthermore, even amounts of oxides as low as 0.2 mol% has a significant outcome.

Barkhordarian *et al.* (2004) investigated the effect of N$_2$O$_5$ oxide on Mg-based nanocrystalline hydrides after 120 h of ball milling. They realized that absorption kinetics is nearly independent of the catalyst content and that 0.05 mol% Nb$_2$O$_5$ yields the full hydrogen absorption of 7 wt% within 60 s. Oelerich *et al.* (2001) studied the effects of various transition metal oxides as catalysts under the same milling conditions. They found that the composite material containing Fe$_3$O$_4$ showed the fastest kinetics, followed by V$_2$O$_5$, Mn$_2$O$_3$, Cr$_2$O$_3$ and TiO$_2$. Sub Lee *et al.* (2004) noticed that the reactive grinding of Mg with CoO and the hydriding–dehydriding cycling increase the H$_2$ sorption rates. The influence of reactive grinding of Mg with Fe$_2$O$_3$ was investigated by Song *et al.* (2005). They demonstrated that increase in the H$_2$ sorption rates is caused by easy nucleation originated from formed defects on the surface of the Mg particles, and by contrast, by reduction of the particle size of Mg, which means that diffusion distances of hydrogen atoms are shorten.

In the present study, the effect of natural material diatomite (as additive) on the hydrogen storage behaviour of MgH$_2$ was investigated. Diatomite as sedimentary rock, mainly formed from SiO$_2$, Fe$_3$O$_4$ and Al$_2$O$_3$, is acknowledged for its unique combination of physical and chemical properties such as high porosity, small particle size, large surface area and good absorption properties (Karatepe *et al.*, 2004). The leading idea was to preserve the diatomite-specific porous microstructure and to study its influence on the desorption behaviour on MgH$_2$, so the two-step milling procedure was performed. Decreasing of MgH$_2$ particle size has been achieved during

10 h of milling, whereas the mixture was obtained by additional 1 h of milling.

Experiment

MgH$_2$ (60 μm particle size, containing 5 wt% Mg as impurity, from Alfa Aesar) and diatomite from coal mine Kolubara were processed by ball milling in a Turbula Type T2C Mixer. Both milling steps were performed under argon using a ball-to-powder (BPR) ratio of 10:1. Prior to milling with diatomite, pure MgH$_2$ was pre-milled for 10 h, then the mixture was prepared by additional 1 h of milling with 10 wt% of diatomite. All handling of powders, including milling, were performed inside a glove box under a continuously purified Ar atmosphere.

Morphological and microanalytical characterization was carried out by SEM analyses using JEOL JSM 6460LV (JEOL, Tokyo, Japan) and Oxford Instrument INCA-X-sight (Oxford Instruments, Eynsham, UK) operating at 25 kV. To evaluate the particle size and distribution, the as-milled powders were sonicated in ethanol for 15 min and then a drop of the suspension was posed to dry on a carbon tape. The particle size distribution was evaluated by analyzing the digital micrographs with the software package ImageJ (http://rsb.info.nih.gov/ij/). The average particle size of milled MgH$_2$ was 30 μm.

The microstructure of the powders was characterized by X-ray powder diffraction measurements (XRD) on a Philips 1050 X-ray diffractometer (Philips, Amsterdam, the Netherlands) using Ni-filtered Cu Kα radiation and Bragg-Brentano focusing geometry. The patterns were taken in the 5–90° 2θ range with the step length of 0.05° 2θ and exposure time of 5 s per step.

Thermal behaviour of the samples was studied by DSC technique (DSC 151R Setaram Instruments, Setaram Inc., Pennsauken, NJ, USA) operating in temperature range 293–

773 K under Argon atmosphere at a constant heating rate of 15°C min^{-1}.

Results and discussion

Figure 1 represents XRD patterns of milled MgH$_2$ and MgH$_2$-diatomite composite. In both samples, the X-ray diffraction peaks of β-MgH$_2$ were observed, whereas there were no peaks corresponding to γ-MgH$_2$. The diffraction maxima related to SiO$_2$ is present in the composite. Both samples show peak broadening caused by refinement of the average crystallite size and increase in the strain during milling. The crystallite size and microstrain were evaluated using the Rietveld method implemented in the MAUD software package (Lutteroti & Scardi, 1990). The crystallites of tetragonal β-MgH$_2$, whose size in the unprocessed material is larger than 100 nm, were fragmented down to the nanometric range (12 nm) in both composite and milled MgH$_2$. The crystallite size of SiO$_2$ was found to be 4 nm. The microstrain contribution induced by high-energy ball milling, for both MgH$_2$ and SiO$_2$, were 0.5 and 0.2, respectively.

Cylindraceous, porous particles of raw diatomite, which are mostly SiO$_2$, with particle sizes ranging from 10 to 50 μm, can be clearly observed in the SEM micrograph shown in Fig. 2(a). The rod-like particles mainly formed of iron and aluminum oxide can be noticed in Fig. 2(b). Figure 3 represents the micrographs of MgH$_2$-diatomite composite.

It is well known that the oxides are brittle and can be easily pulverized during mechanical milling, but one can notice that the porous texture of diatomite (which is a mixture of oxides) is not completely damaged after ball milling. Cylindraceous diatomite particles are still present in the sample, whereas rod-like particles are partially pulverized during 1 h of milling.

The added oxides in the form of diatomite and/or their pulverization during mechanical grinding may help the particles of MgH$_2$ to become finer. Indeed, it can be noticed that MgH$_2$ particles in the composite are actually formed by the agglomeration of smaller particles, which often exhibit a platelet-like shape.

The DSC curves of MgH$_2$ milled for 10 h and the MgH$_2$-diatomite composite are showed in Fig. 4. As a general behaviour, the hydrogen desorption curves present two endothermic peaks. Milled MgH$_2$ exhibits high-temperature maxima at 703 K and a small shoulder at 682 K. The results obtained by Varin *et al.* (2006) show that two factors determine the hydrogen desorption temperature of MgH$_2$ within a certain nanometric grain size range: the particle size and the presence of metastable γ-MgH$_2$ phase. The γ-MgH$_2$ always shows a lower DSC desorption temperature than β-MgH$_2$ (Gennari *et al.*, 2001), but there is loss of thermodynamic data for γ-MgH$_2$, so one can only guess that it may have lower enthalpy of formation than β-MgH$_2$.

If we take into account the particle size, most of the available literature indicates indirectly that smaller particle
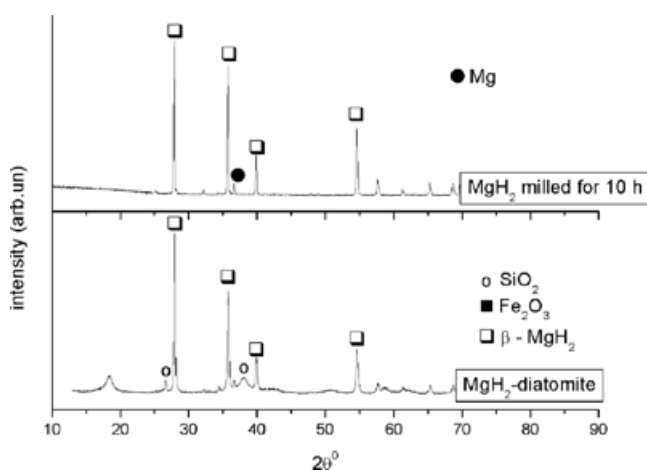

Fig. 1. XRD diffraction patterns of milled MgH$_2$ (up) and MgH$_2$–diatomite (down). Both samples show peak broadening caused by refinement of the average crystallite size and increased strain during milling.
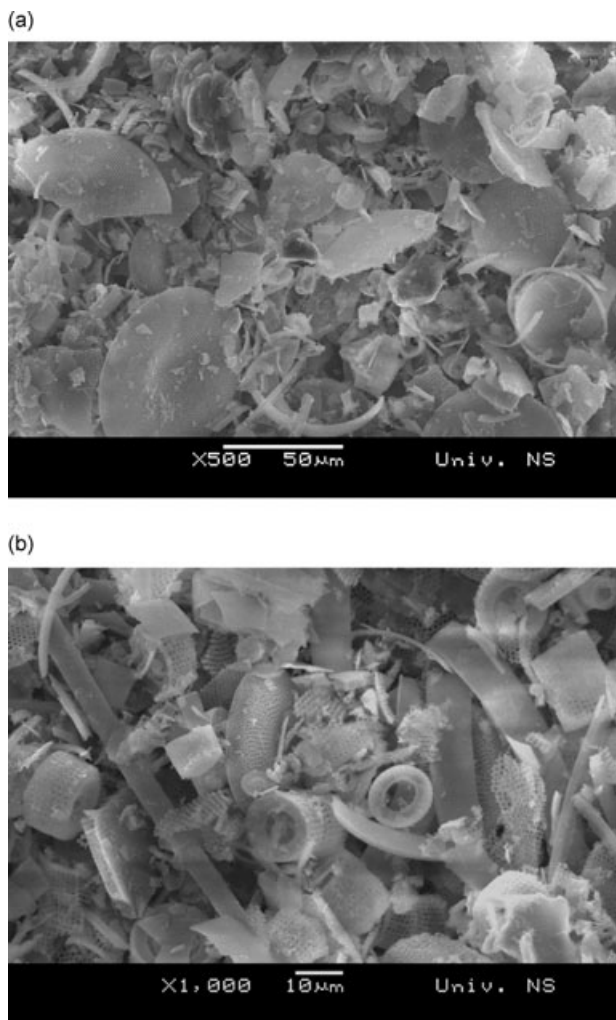
(a)

(b)

Fig. 2. SEM micrographs of raw diatomite. Cylindraceous porous particles (a) and rod-like (b) particles can be observed.

Fig. 3. SEM micrographs of MgH$_2$–diatomite composite showing a porous structure.

Fig. 4. The DSC traces of pure MgH$_2$ milled for 10 h (solid line) and MgH$_2$–diatomite composite (dash line). As general behaviour, the hydrogen desorption curves presents two endothermic peaks shifted to the lower temperature in comparison with pure nonmilled MgH$_2$ ($T_p = 720$ K).

size could have a beneficial effect on both desorption kinetics and desorbed capacity (Selvam *et al.*, 1986; Hout *et al.*, 1999; Bassetti *et al.*, 2004; Bassetti *et al.*, 2005; Varin *et al.*, 2006). In particular, Selvam *et al.* (1986) pointed out the fact that in the dehydriding step of coarse particles, progressively formed Mg surface layer, may function as the diffusion barrier to the hydrogen desorption from MgH$_2$. In small MgH$_2$ particles, the Mg phase can be formed at the same time all through the material; consequently, the entire process of desorption is governed by fast hydrogen diffusion rather than slow Mg–MgH$_2$ boundary movement.

According to Bassetti *et al.* (2005), the desorption process is directed by the morphology of the catalyst dispersion on the surface of the magnesium matrix, which depends on the processing conditions and blend composition. To achieve lower desorption temperatures, the catalyst should disperse homogeneously in micron-size particles throughout
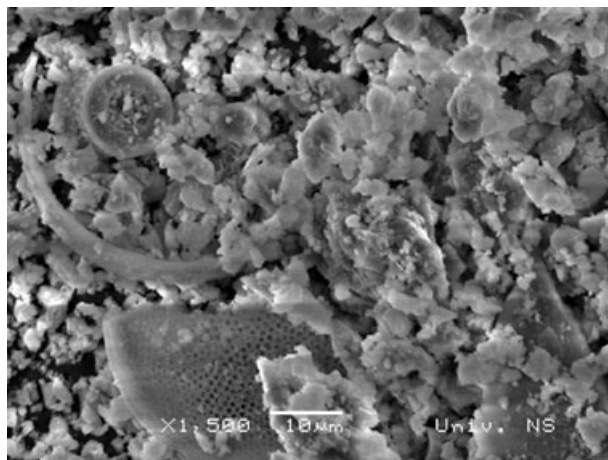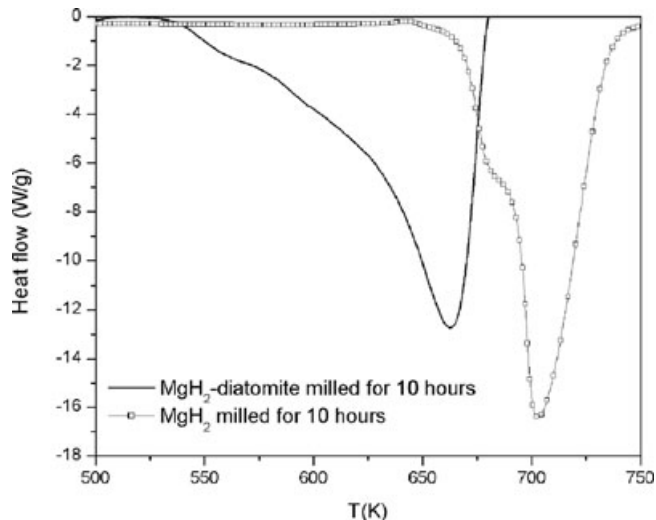
the structure. These smaller particles will provide a larger surface area for the recombination of hydrogen molecules.

As in our case, XRD analysis did not show the presence of γ-MgH$_2$, and the two-step desorption can be attributed, according to prior argumentation, to the decreased particle size of β-MgH$_2$. Also, both temperature maxima in the MgH$_2$–diatomite composite are shifted to the lower temperatures (661 and 473 K). In addition, the quite wide peak at 661 K indicates large amount of released hydrogen, and it might be ascribed to the preserved porous microstructure of diatomite (see Fig. 3) and/or homogenous dispersion of catalyst in the MgH$_2$ matrix surface. To obtain fast desorption in composites based on MgH$_2$, as noted by various research groups (Gross *et al.*, 1998; Bassetti *et al.*, 2005), homogenous dispersion of catalyst in the
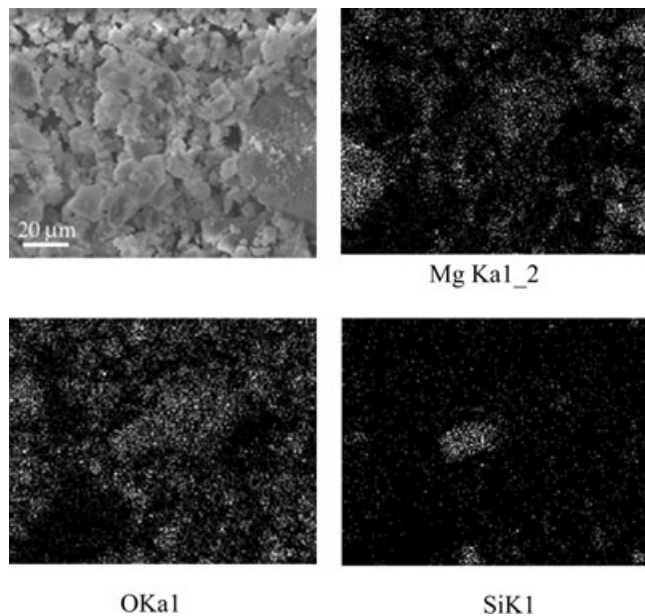
Fig. 5. The chemical maps relative to the same sample area of MgH$_2$–diatomite composites show that oxides are not well dispersed in the MgH$_2$ matrix.

MgH$_2$ matrix surface is required. Nevertheless, the mapping analysis of the MgH$_2$–diatomite composite represented in the Fig. 5 shows that oxides are not well dispersed in the MgH$_2$ matrix. As previously reported, oxides may have a catalytic function owing to a partial or total reduction of oxides to native metal during mechanical milling (Oelerich *et al.*, 2001). But as it was shown by the XRD data given in Fig. 1, nanosized oxides are not reduced during mechanical milling, and consequently such hypothesis is not applicable in our case. If we take into account that only transition metal oxides with multiple valences are expected to have a catalytic effect (Oelerich *et al.*, 2001), the enhanced desorption characteristic obtained with diatomite cannot be explained by catalytic effect. This indicates that the preserved porous microstructure of diatomite plays the main role in the enhancement of desorption properties.

Conclusion

The influence of porous diatomite structure on the desorption properties of MgH$_2$ was investigated by DSC. To preserve the particular microstructure of diatomite, the specific two-step ball milling procedure was followed. It was noticed that since the additive was not homogeneously dispersed in the sample and there was no reduction of oxides to native metal during mechanical milling, the decrease in desorption temperature is not a result of the catalytic effect of mixed metal oxides (diatomite), but that the fine porous microstructure of the

composite plays a foremost role. This is the reason why diatomite cannot be considered as a catalyst but only as an additive.

Acknowledgement

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