

THE EFFECTS OF MICROSTRUCTURAL MODIFICATION BY MECHANICAL MILLING ON HYDROGEN DESORPTION FROM MAGNESIUM HYDRIDE

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Abstract

Nanostructured hydrides fabricated by mechanical (ball) milling offer a promising alternative to hydrogen storage in compressed or liquid form. However, ball milling brings about both beneficial and detrimental effects to their hydrogen desorption characteristics. These effects have been studied in the ball milled magnesium hydride, MgH₂. A beneficial effect is that the refinement of the hydride powder particle size and the γ -MgH₂ phase residing within the powder particles, acting additively, are responsible for a substantial reduction of hydrogen desorption temperature of MgH₂ hydride. A detrimental effect is a reduction of the hydrogen storage capacity after nanostructuring of MgH₂ by ball milling. Both effects are presented and discussed.

In particular DSC hydrogen desorption curves at the heating rate of 4°C/min of the ABCR powder as received, milled in hydrogen for (a) 0.25 to 5h and (b) 10 and 20h and finally cycled, XRD patterns of MgH₂ (Tego Magnan®) powders milled continuously for 100h, desorption curves under 0.1 MPa H₂ at various temperatures of commercial MgH₂ powder Tego Magnan® milled continuously for 20h are presented in the paper.

Keywords: *automotive, hydrogen fuel for fuel cells, magnesium hydride, mechanical milling, hydrogen desorption*

1. Introduction

Due to the looming global warming and eventual depletion of fossil fuels in the next 30 to 50 years, alternative energy sources and fuels must be urgently sought [1]). For example, the Toyota

Prius 2006 which is an electric/gasoline hybrid, perceived by the public as the “greenest” automobile in Canada, still produces as much as 1968 kg CO₂ per year [2].

The most attractive alternative fuel is hydrogen. However, one of the serious obstacles to the hydrogen usage in transportation is onboard H₂ storage. Solid state hydrides have the highest volumetric densities of hydrogen (80-150 kgH₂m⁻³) [3,4] which exceed those found in common hydrogen storage systems such as high pressure gas cylinders and cryogenic tanks for liquid hydrogen [3-5] and they provide 100% pure H₂. However, their absorption/desorption temperatures are still too high for supplying Proton Exchange Membrane (PEM) fuel cell (FC) vehicles where H₂ must be liberated at temperatures compatible with the waste heat of the PEM FC (roughly about 80-100°C range) [3-5].

A simple, fully reversible [3-5] metal hydride MgH₂ (magnesium hydride or “dihydride”) is widely available, easy to handle, has a practical hydrogen capacity of ~7.0wt.% (at 95% purity) which is near the 2010 target of 6.5wt.%H₂ for the FreedomCar program of the Department of Energy (USA) [3-8]. However, its hydrogen sorption/desorption temperature is around 400°C, too high for a PEM FC. In the last few years, we have been using advanced mechanical (ball) milling techniques to achieve substantial nanostructuring of MgH₂ which could reduce its sorption/desorption temperature. In the present paper we present some recent advances which we have made in the fundamental understanding of structural modifications achieved by mechanical (ball) milling of MgH₂ and their effect on its hydrogen desorption characteristics.

2. Experimental

A specialized magneto-mill, Uni-Ball-Mill 5 (A.O.C. Scientific Engineering Pty Ltd., Australia) [9-11] has been used for the fabrication of nanostructured (nanocrystalline) magnesium hydride (MgH₂). Two types of MgH₂ powders were used: first Tego Magnan® from Degussa-Goldschmidt; ~95wt.% purity, the remaining Mg and second from ABCR GmbH&Co.KG sold under the trade name MG-5026; average purity ~98%, the remaining Mg. More extensive details of milling procedures can be found in a number of recent references [12-16].

Morphological examination of powders was conducted with high-resolution, field emission SEM (FE SEM) LEO 1530 equipped with integrated EDAX Pegasus 1200 EDS/OIM. The nanograin (crystallite) size of phases residing in the milled powders was calculated from the broadening of their respective XRD peaks. More details can be found in [12-16].

The thermal behaviour of powders was studied by Differential Scanning Calorimetry (DSC) (Netzsch 404) of ~20 mg powder sample with heating rate of 4°C/min and argon flow rate of 16ml/min. The samples were tested within maximum two weeks from the completion of milling to avoid environmentally-induced aging phenomena [13].

3. Results and discussion

Fig.1 shows the DSC curves of MgH₂ powders ball milled for various times. The endothermic hydrogen desorption peaks are broad and have characteristic shoulders which suggest overlapping of two peaks. The shoulder temperatures are designated LT and the peak maxima are designated HT in Fig.1. Both LT and HT temperatures decrease systematically with increasing milling time. Subsequently, the milled powders were thermally cycled in hydrogen as follows: heating to 325°C for ~15min under 3.4MPa H₂ to prevent desorption and then 2 desorptions at 325°C under 0.1MPa H₂ pressure for ~4700s with intermediate annealing under pre-vacuum at 350°C for 15min and absorption at 350°C under 3.4MPa H₂ for 30min. The mean particles sizes calculated as Equivalent Circle Diameter (ECD) [15-16] after milling and cycling are listed in Table 1. Within the experimental scatter the mean particle sizes after cycling do not differ from those after milling.

The cycled samples were again tested in DSC and the corresponding curves shown in Fig.2 are smooth and symmetrical without any shoulders. The desorption peaks are shifted back to higher temperatures while they still show a systematic decreasing trend with increasing milling time.

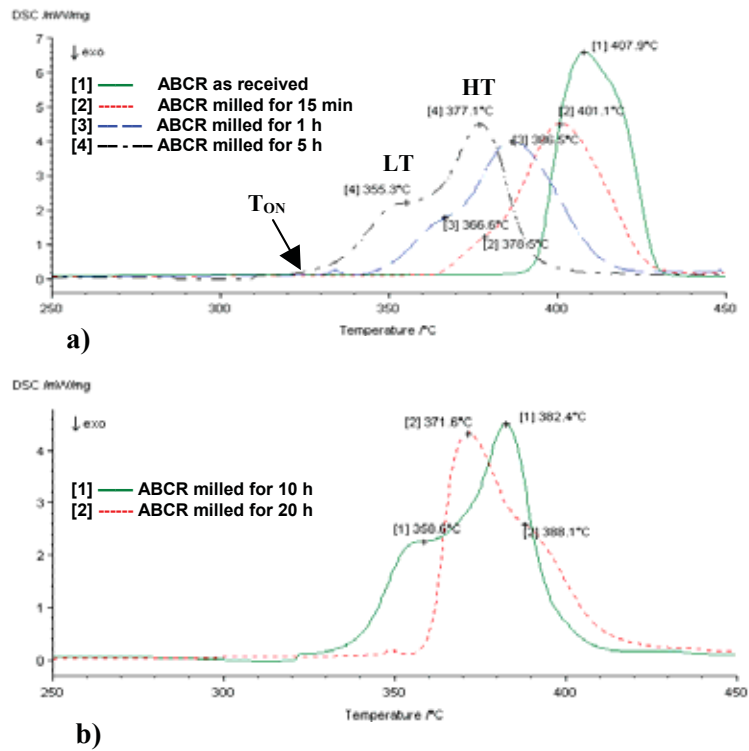


Fig.1. DSC hydrogen desorption curves at the heating rate of 4°C/min of the ABCR powder as received and milled for (a) 0.25 to 5h and (b) 10 and 20h under HES57 mode in hydrogen

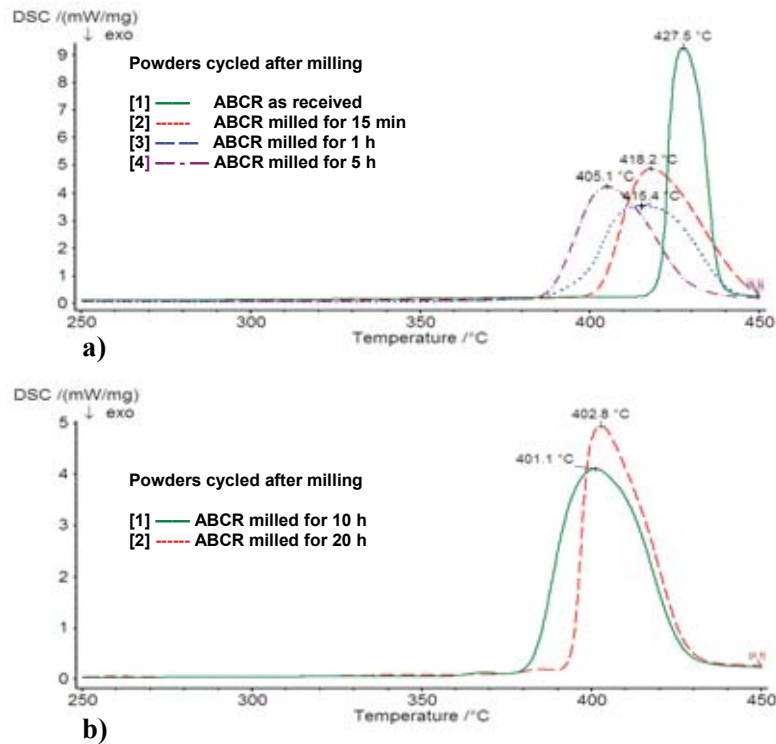


Fig.2. DSC hydrogen desorption curves at the heating rate of 4°C/min of the ABCR powder as received, milled in hydrogen for (a) 0.25 to 5h and (b) 10 and 20h and finally cycled

Fig.3a and b show XRD patterns of milled and cycled samples, respectively. As milled powders contain both β - and γ -MgH₂ hydride phases (Fig.3a) where the latter is a high pressure polymorphic form of MgH₂ [17]. Thermal cycling eliminates γ -MgH₂ from the microstructure of milled powders (Fig.3b). As reported by Gennari et al. [18] the LT shoulder observed in DSC curves of milled MgH₂ powders in Fig.1 is most likely due to the hydrogen desorption from the γ -MgH₂ phase. Elimination of γ -MgH₂ after thermal cycling makes the DSC curves smooth since they now correspond only to the hydrogen desorption from β -MgH₂ (Fig.2).

Tab.1. The mean particle size (ECD) of ABCR powder after milling and after subsequent cycling

Milling time (h)	After milling		After cycling	
	Mean particle size (ECD) (nm)	Standard deviation (nm)	Mean particle size (ECD) (nm)	Standard deviation (nm)
As received	40973	21116	35279	21894
0.25	1110	959	1308	586
1	977	806	961	663
5	850	643	989	512
10	844	571	951	614
20	854	634	917	430

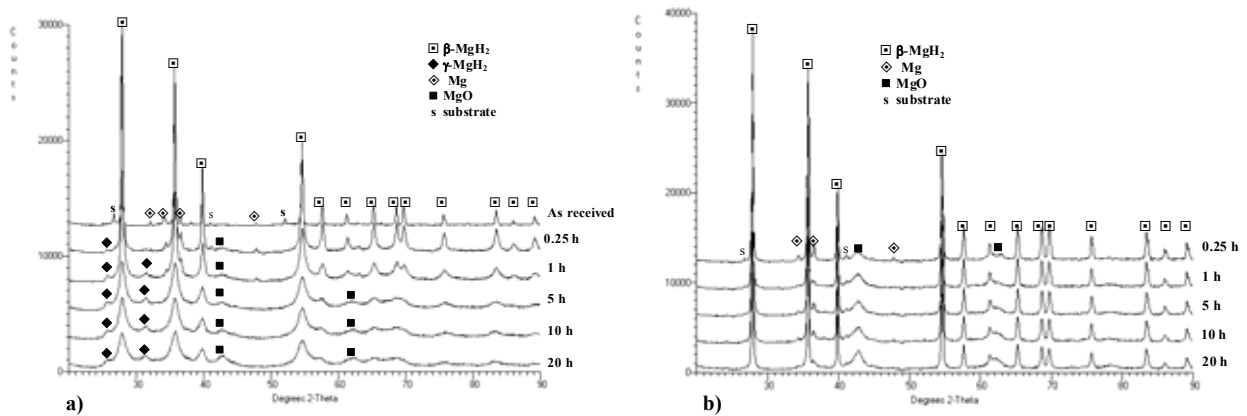


Fig. 3. XRD patterns of (a) milled ABCR powders and (b) the same powder after cycling as described in the text

The DSC onset (T_{ON}) and peak maximum (T_{peak}) temperatures from Fig.1 and 2 are plotted in Fig.4a and b, respectively, as a function of particle size (corresponding grain size of β -MgH₂ is also shown beside each data point). The plotted curves for cycled samples in Fig.4a and b which correspond to the hydrogen desorption from β -MgH₂ are shifted up with respect to the milled samples which correspond to the desorption from a phase mixture of β -MgH₂+ γ -MgH₂. The shape of the as milled and cycled curves is very similar, i.e. gradual decrease in the first stage and subsequent fast decrease after reaching a critical value of the particle size (~1000nm). The grain size of the β -MgH₂ phase does not seem to affect the DSC hydrogen desorption temperature in any systematic manner. Accordingly, based on this quantitative evidence it can be concluded that two microstructural factors such as the γ -MgH₂ phase residing within the powder particles and refined powder particle size, acting additively, contribute to a substantial reduction of hydrogen desorption temperature of MgH₂ hydride as observed in DSC.

A substantial apparent reduction of hydrogen desorption temperature with decreasing particle size as obtained by ball milling is a very beneficial effect although the reduced onset and peak hydrogen desorption temperatures are still slightly higher than 300°C, i.e. too high for supplying a PEM FC. However, ball milling and resulting nanostructuring of MgH₂ also brings about a detrimental effect which is a reduction in the hydrogen storage capacity of the milled powders. The purity-corrected hydrogen capacity of the Tego Magnan® MgH₂ powder is around 7.2wt.% at 95% purity. This capacity is in practical terms obtained by hydrogen desorption from unmilled commercial Tego Magnan® powder at the temperature range 350-420°C. However, as can be seen in Fig.5 the capacity obtained after desorption at such high temperatures as 350 - 400°C is less than the purity-corrected hydrogen capacity for this powder. As shown by XRD patterns in Fig.6 after desorption at all three temperatures there are high- intensity peaks of newly-formed Mg and small but sharp peaks of retained MgH₂ discernible on the XRD pattern.

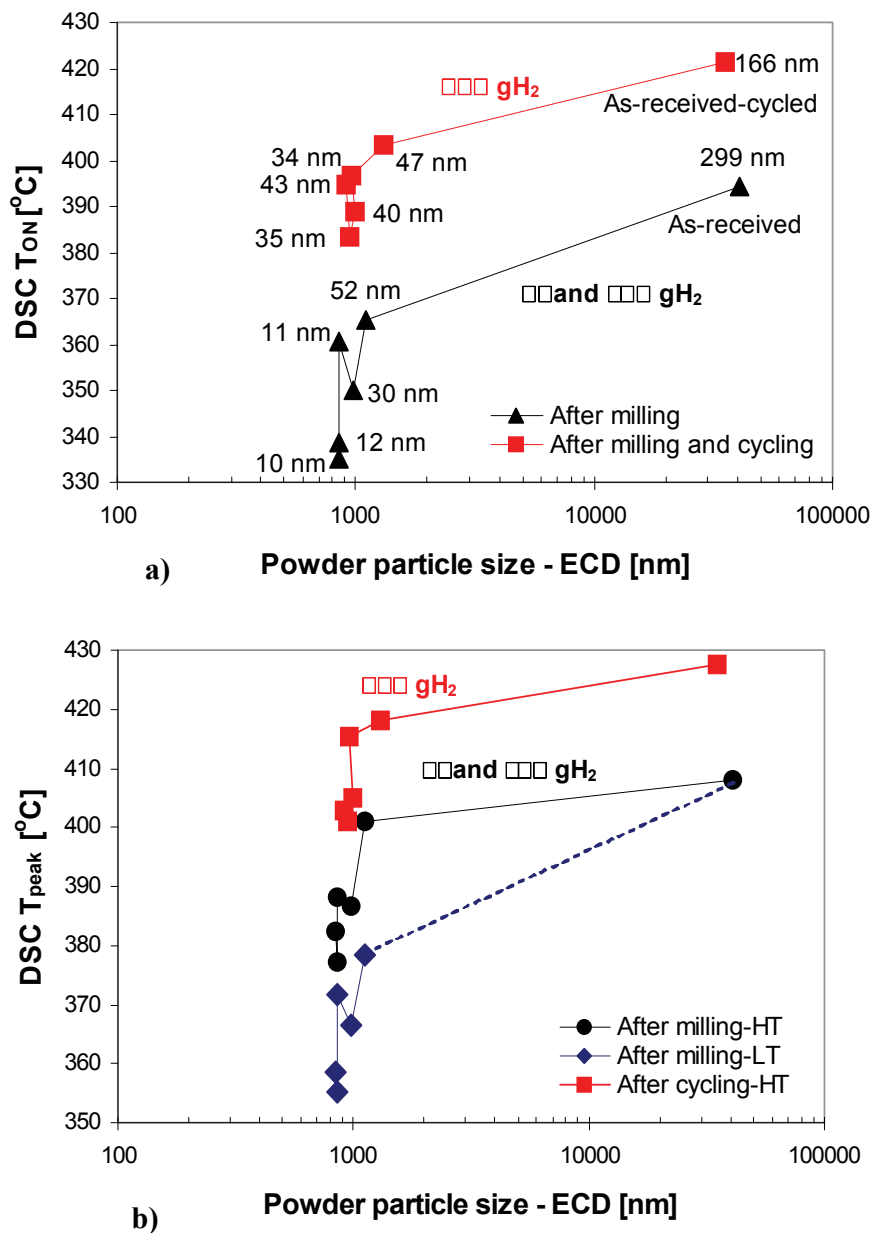


Fig.4. Changes of DSC hydrogen desorption temperatures from Fig.1&2 as a function of particle size (ECD) of milled and cycled ABCR powder. Numbers beside each data point indicate the grain size of β -MgH₂. (a) Onset temperature (T_{ON}) and (b) peak temperatures (T_{peak}). Standard deviations for the mean particle size (ECD) from Tab.1 are omitted for clarity

Most likely, this is due to the following phenomena. First, inevitably about 18% of γ -MgH₂ is always formed during milling [19] due to the transformation of β -MgH₂ into γ -MgH₂ (Fig.3a). However, during subsequent high temperature desorption or cycling this orthorhombic hydride phase quickly disappears (Fig.3b).

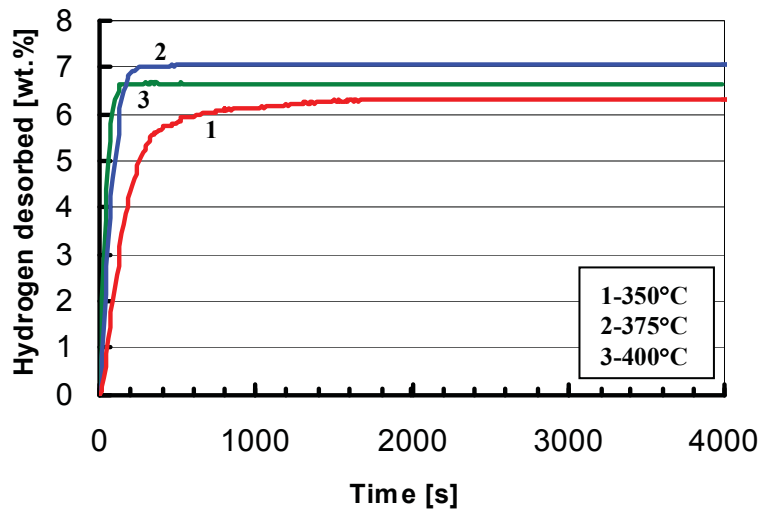


Fig.5. Hydrogen desorption curves under initial hydrogen pressure of 0.1 MPa at three different temperatures of Tego Magnan® milled continuously in argon for 100h under IMP68 mode (strong impact mode with two magnets at 6 and 8 o'clock position; for details see [9-16])

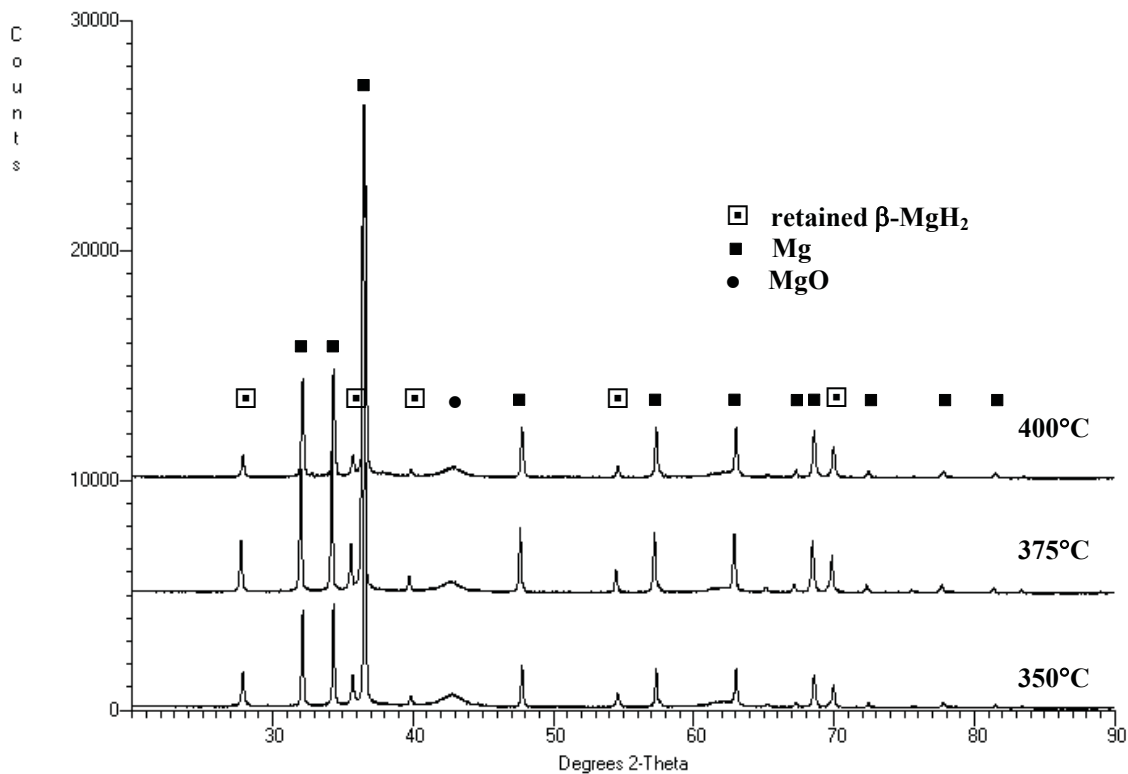


Fig.6. XRD patterns of MgH₂ (Tego Magnan®) powders milled continuously for 100h under IMP68 mode from Fig.5 and subsequently desorbed directly after milling in a Sieverts-type apparatus under initial hydrogen pressure of 0.1 MPa at various temperatures

According to Gennari et al. [18] the initial decomposition of γ phase produces synergetic effects during hydrogen desorption that stimulate β -MgH₂ decomposition by creating a volume

contraction which, in turn, generates stresses acting on β -MgH₂. Conversely, one may argue that if the γ phase decomposes too quickly then the β phase may become too stable and small amounts of it may persist even up to high desorption temperatures. Second, during desorption of a milled MgH₂ powder there always occurs a simultaneous growth of nanograins of β -MgH₂ (Table 2). Since particle size is not changed during desorption, one may hypothesize that the growth of nanograins within the β -MgH₂ particles might somehow decelerate the decomposition of β -MgH₂.

Tab.2. Grain size of β -MgH₂, Mg and retained β -MgH₂ in the Tego Magnan® powder after milling and desorption at various temperatures (calculated from Fig.6).

Powder	Grain size(nm)	Strain (%)	R ²	Number of peaks
MgH ₂ - milled	14	0	0.9964	7
350°C (Mg)	86	8.2×10 ⁻⁴	0.9838	3
350°C (MgH ₂)	55	0	0.9947	4
375°C (Mg)	99	6.6×10 ⁻⁴	0.9997	3
375°C (MgH ₂)	80	0	0.9973	5
400°C (Mg)	78	5.4×10 ⁻⁴	0.9948	6
400°C (MgH ₂)	62	0	0.9948	6

Discontinued ball milling when the milling vial is periodically opened in due course of milling apparently degrades the desorption properties of milled MgH₂ powder even further as shown in Fig.7b. In comparison to continuously milled powders in Fig.7a the kinetics at 325°C of discontinuously milled powders in Fig.7b is much worse.

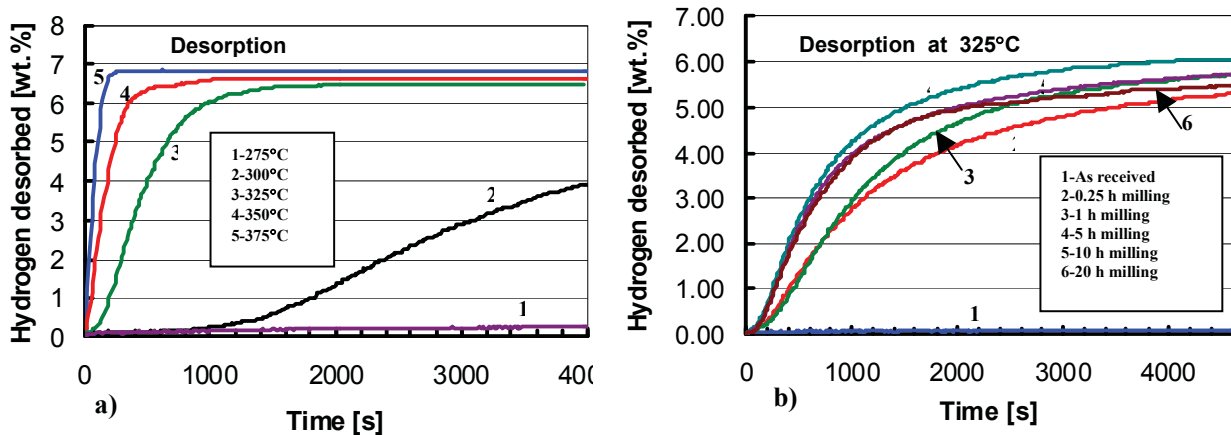


Fig.7. Desorption curves under 0.1 MPa H₂ (a) at various temperatures of commercial MgH₂ powder Tego Magnan® milled continuously for 20h under IMP68 mode [9-16] (in argon) (b) at 325°C of ABCR powder pre-milled discontinuously for various time durations under HES57 mode [9-16] (in hydrogen)

4. Conclusions

Nanostructuring of magnesium hydride (MgH₂) by high-energy ball milling brings about both beneficial and detrimental effects to their hydrogen desorption characteristics. An experimentally observed beneficial effect is that the apparent hydrogen desorption temperature, as measured in a DSC test, decreases with decreasing particle size of a ball milled hydride powder. There are two factors acting additively that contribute to this behavior: the refinement of the hydride powder particle size and the γ -MgH₂ phase residing within the powder particles which has lower desorption temperature than β -MgH₂. A detrimental effect is a reduction in the hydrogen storage capacity after nanostructuring of MgH₂ by ball milling.

References

- [1] Scott, D. S., *Fossil sources running out is not the problem*, Int. J. Hyd. Energy 30, 1-7, 2005.
- [2] Natural Resources Canada; Fuel Consumption Ratings 2006.
- [3] Schlapbach, L., Züttel, A., *Hydrogen-storage materials for mobile applications*, Nature 414 353-358, 2001.
- [4] Ritter, J. A., Ebner, A. D., Wang, J., Zidan, R., *Implementing a hydrogen economy*, Materials Today 6(9), 18-23, 2003.
- [5] Züttel, A., *Materials for hydrogen storage*, Materials Today 6(9)(2003)24-33, 2003.
- [6] Slattery, D. K., Hampton, M. D., *Complex hydrides for hydrogen storage*, Proceedings of the 2002 U.S. D.O.E. Hydrogen Program Review NREL/CP-610-32405, 2002.
- [7] Grochala, W., Edwards, P. P., *Thermal decomposition of the non-interstitial hydrides for the storage and production of hydrogen*, Chemical Reviews 104, 1283-1315, 2004.
- [8] Sandrock, G., *A panoramic overview of hydrogen storage alloys from a gas reaction point of view*, J. Alloys Compd. 293-295, 877-888, 1999.
- [9] Calka, A., Radlinski, A. P., *Universal high performance ball-milling device and its application for mechanical alloying*, Mater.Sci.Eng. A 134, 1350-1353, 1991.
- [10] Patents: WO9104810, US5383615, CA2066740, EP0494899, AU643949.
- [11] Calka, A., Varin, R. A., *Application of Controlled Ball Milling in Materials Processing*, Proc. Int. Symp. on Processing and Fabrication of Advanced Materials IX (PFAM-IX), T.S. Srivatsan, R.A. Varin, M. Khor (Eds.) (ASM International, Materials Park, OH, pp.263-287, 2001.
- [12] Li, S., Varin, R. A., Morozova, O., Khomenko, T., *Controlled mechano-chemical synthesis of nanostructured ternary hydride Mg_2FeH_6 under low-energy impact mode with and without pre-milling*, J. Alloys Compd. 384, 231-248, 2004.
- [13] Varin, R. A., Li, S., Calka, A., *Environmental degradation by hydrolysis of nanostructured β - MgH_2 hydride synthesized by controlled reactive mechanical milling (CRMM) of Mg*, J. Alloys & Compd. 376, 222-231, 2004.
- [14] Varin, R. A., Li, S., Wronski, Z., Morozova, O., Khomenko, T., *The effect of sequential and continuous high energy impact mode on the mechano-chemical synthesis of nanostructured complex hydride Mg_2FeH_6* , J. Alloys Compd. 390, 282-296, 2005.
- [15] Varin, R. A., Czujko, T., Chiu, Ch., Wronski, Z., *Particle size effects on the desorption properties of nanostructured magnesium dihydride (MgH_2) synthesized by controlled reactive mechanical milling (CRMM)*, J. Alloys Compd. 424, 356-364, 2006.
- [16] Varin, R. A., Czujko, T., Chiu, Ch., Wronski, Z., *Particle size, grain size and γ - MgH_2 effects on the desorption properties of nanocrystalline commercial magnesium hydride processed by controlled mechanical milling*, Nanotechnology 17, 3856-3865, 2006.
- [17] Bastide, J.-P., Bonnetot, B., Létouffé, J.-M., Claudy, P., *Polymorphisme de l'hydrure de magnésium sous haute pression*, Mat. Res. Bull. 15, 1779-1787.
- [18] Gennari, F. C., Castro, F. J., Urretavizcaya, G., *Hydrogen desorption behavior from magnesium hydrides synthesized by reactive mechanical alloying*, J. Alloys Compd. 321, 46-53, 2001.
- [19] Huot, J., Liang, G., Boily, S., Van Neste, A., Schulz, R., *Structural study and hydrogen sorption kinetics of ball-milled magnesium hydride*, J. Alloys Compd. 293-295, 495-500, 1999.