

H₂ sorption performance of NaBH₄–MgH₂ composites prepared by mechanical activation

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Abstract

The current research on solid state hydrogen storage materials for on-board applications is focused on *reactive hydrides composites* (RHC), i.e. systems based on the improvement of the dehydrogenation thermodynamic of a complex hydride when one (generally the light hydride MgH₂) or more hydrides take part to the reaction. The extent of the destabilization, as well as the sorption characteristics of the composites, strongly depends on the structural and nanostructural properties of the constituent hydrides, which are in turn affected by the preparation route. The aim of this work is to evaluate the influence of different mechanical activation conditions on the storage properties of NaBH₄ – MgH₂ composites, up to now scarcely explored in literature. The first results regard composites with 2:1 and 1:2 stoichiometry milled under different atmosphere (Ar or H₂). X-ray powders diffraction analysis shows that milling does not lead to the formation of any new phase, but it reduces the average crystallite size of the powders down to nanometric scale. All the mixtures release an H₂ amount close to the theoretical value expected for the full dissociation of both the hydrides and much higher than the target fixed by the US Department of Energy for on-board application. The thermal programmed desorption profiles of the mixtures clearly show two steps, with MgH₂ dissociating first and with higher rate and NaBH₄ gradually dehydrogenating at temperatures close to 400°C. Concerning the 2:1 stoichiometry, when the samples are processed under Ar the two dehydrogenation processes are characterized by a lower starting temperature but also by a lower average rate with respect to the sample milled in H₂. The 1:2 sample milled under Ar shows the best kinetic performance. Unfortunately, also for this mixture more than 10 h are required to obtain full desorption at a temperature as high as 450°C.

Keywords: *solid state H₂ storage, reactive hydride composites (RHC), high energy mechanical milling, sorption kinetics, dehydrogenation enthalpy.*



1 Introduction

The ever-increasing demand for energy all over the world, coupled with the depletion of the fossil fuels and the pollution problems due to their use, makes the establishment of a clean and sustainable energy system a compelling need. The use of the “green” fuel hydrogen seems a good alternative to gasoline (Züttel [1]). Although, in the long term, the ultimate technological challenge is the large-scale hydrogen production from renewable sources, the pressing issue is how to store hydrogen efficiently for on-board fuel cell vehicles. The H_2 solid state storage in nanocomposites is considered the safest and most efficient solution: in recent years, increased efforts are under way to develop materials with reversible storage properties meeting the targets for on-board applications fixed by the US Department of Energy DOE [2] (for the year 2010: • gravimetric storage capacity = 60 g H_2 /1 kg storage material, i.e. 6 wt %, and volumetric storage capacity = 60 g H_2 /dm³; • minimum/maximum delivery temperature - 40°C/+85°C at H_2 pressure > 1.5 bar, as required by the protonic exchange membrane fuel cells to couple with the H_2 tank; • invariance of the performance for at least 1000 charging/discharging cycles; • charging rate = 1.2 kg H_2 min⁻¹ and discharging rate = 0.02 g H_2 s⁻¹/kW fuel cell for a system storing 5 kg H_2).

To reach these goals, the research is currently focused on complex ternary hydrides such as alanates, amides and borohydrides (Chen and Zhu [3]). In particular, the alkaline borohydrides $NaBH_4$ and $LiBH_4$ seem particularly appealing since they are characterized by volumetric hydrogen densities of about 120 g H_2 /dm³ and theoretical gravimetric capacity as high as 10.8% and 18.3 wt % respectively (Züttel et al. [4], Orimo et al. [5]). Unfortunately, these compounds are known to be very stable (Fedneva et al. [6], Stasinevich and Egorenko [7], Ostroff and Sanderson [8], Züttel et al. [9]): they start decomposing at temperatures close to 400°C, and below 600°C they release only half of their hydrogen content with unsuitable decomposition rates (more than 20 h for $LiBH_4$ and 100 h for $NaBH_4$). Moreover, to reverse the sorption reactions is a significant challenge because of the extremely rigorous conditions required in terms of both pressure and temperature (H_2 pressure of 350 bar and temperatures higher than 600 °C, Stasinevich and Egorenko [7], Orimo et al. [10]). In the last years, many efforts have been made to improve both the thermodynamic and the kinetic characteristics of $LiBH_4$ desorption by addition of suitable catalyzing/destabilizing agents. A promising solution seems the preparation of the so called “reactive hydrides composites” (RHC) systems (Barkhordarian et al. [11], Vajo et al. [12]), made of the borohydride, the light hydride MgH_2 (Dornehim et al. [13], Vajo et al. [14,15]), and eventually other complex hydrides such as $LiAlH_4$ and/or $LiNH_2$ (Pinkerton et al. [16], Sudik et al. [17], Yang et al. [18,19]). The borohydride reacts with the destabilizing hydride or with its dehydrogenation product, leading to the formation of a stable discharged compound (the general reaction scheme being $AH + MBH \rightarrow AB + MH$). Thanks to this exothermic reaction, the system desorption enthalpy decreases with respect to that of the pure borohydride and this same phase desorbs at a



lower temperature. Note that using a hydrogen active specie as destabilizing agent allows one to keep a high hydrogen capacity for the system.

Up to now, this solution has been scarcely investigated regarding NaBH_4 (Barkhordarian et al. [20], Czujko et al. [21]). Anyway, NaBH_4 is a good model to investigate the sorption mechanism of the RHC based on alkaline complex hydrides since it is relative cheap and quite stable at the moisture (characteristic satisfying the DOE safety conditions). For this reasons, we started a systematic explorative work concerning the $\text{NaBH}_4 - \text{MgH}_2$ system.

In this paper, the first results on $\text{NaBH}_4 - \text{MgH}_2$ composites with 2:1 and 1:2 stoichiometry are reported. The samples have been prepared by high energy ball milling, a technique based on the application of mechanical forces to powdered specimens that it is widely employed for the preparation of a variety of metastable systems including hydrogen storage materials (Suryanarayana [22], Dornheim et al. [13]). The composites have been processed under different atmosphere (Ar or H_2) and subsequently characterized by X-ray powder diffraction, scanning electron microscopy, sorption volumetric measurements and high pressure calorimetry regarding both their structural properties and their kinetic and thermodynamic storage performance. The final aim of the work is to find the relationships between the preparative parameters, the composition of the mixtures and their storage properties in order to control the former ones to optimize the latter.

2 Experimental details

High purity grade NaBH_4 and MgH_2 powders (325 mesh) were purchased from Aldrich. An amount of 5% mol of hexane (from Aldrich, 99% purity) was added to the reacting mixture as a process control agent. All the samples handling operations described in the following were performed in an MBraun glove – box operating under purified Ar atmosphere (O_2 , H_2O and N_2 contents at ppm levels).

As a general procedure, 8 g of each reacting mixture were sealed in a stainless steel vial together with a single stainless steel ball of 12 g and milled in a commercial Spex Mixer/Mill model 8000 for 15 h. The structural properties of the powders were studied by X-ray powders diffraction (XRPD) using a Bruker D8 diffractometer equipped with Cu K_α radiation, and a graphite monochromator in the diffracted beam. The powders were placed in an X-ray sample holder covered with a Kapton foil in order to avoid oxidation during the analysis. Phase abundance and microstructural parameters were evaluated by least squares fitting refinement procedures based on the Rietveld method [23], employing the MAUD (Materials Analysis Using Diffraction) diffraction/reflectivity analysis software (MAUD program [24], Lutterotti and Gialanella [25]).

The morphological characteristics and the average particle size distribution were evaluated by Scanning Electron Microscopy using a Jeol JSM-6300 SEM. Taking into account the small electrical conductivity of the hydrides, before analysis the powders were fixed on a holder (using a double-sided carbon adhesive tape) and covered with a gold layer deposit. Image treatment analyses



have been performed to determine the particle size distribution, which can be adjusted to a log-normal function.

The sorption profiles were acquired by a volumetric Sievert type apparatus (PCTPro-2000; Setaram & Hy-Energy). 500 mg of sample were heated from room temperature to 450 °C at 2 °C/min and starting H₂ pressure = 0.1 bar (thermal programmed desorption measurement TPD) and then kept in isothermal conditions till desorption was completed (more than 10 h were needed). Subsequently, the samples were re-charged at 450 °C and 50 bar H₂, cooled down to 200 °C in isobaric conditions and discharged again by a second TPD measurement (performed in the same condition of the 1st measurement). The sorption rates corresponding to each reactive step were obtained (in wt % H₂/min) as the ratio between the experimental amount of released H₂ and the time needed for the completion of the process.

The calorimetric measurements were performed in a high pressure differential scanning calorimeter (Sensys DSC, Setaram) equipped with both a gas control panel enabling the acquisition of the calorimetric profiles in isobaric conditions and a two channels gas commutation device (Automation S.r.L, Italy). The measurements were performed by heating about 10 mg of sample from room temperature to 580 °C at 2 °C/min and 3 °C/min and constant H₂ pressure = 0.4 bar.

3 Results and discussion

The hydrogen sorption properties of the investigated materials are expected to strongly depend on the structural destabilization of the reactants. In this connection, in order to increase the kinetic energy delivered to the reactants, different milling conditions were tested for the preparation of the composites, by varying the sphere mass, the engine rotation speed as well as the milling atmosphere (Ar or H₂). In Figure 1 the XRPD (experimental and computed) patterns of three selected mixtures, on which we will focus in this work, are shown, while in Table 1 the results of Rietveld refinement are reported. Irrespective of the milling conditions, only peaks attributable to the two starting hydrides are distinguishable in the patterns within the detection limits of XRPD techniques, indicating that milling induces no chemical reaction between the components of the mixtures. This is testified also by the fact that the calculated phases wt % ratio is coincident with the stoichiometry of the as prepared mixtures.

No significant variation in the lattice parameters of the two phases was observed in comparison with the literature data ($a = 6.162 \text{ \AA}$ for NaBH₄ - Abrahams and Kalnajs [26]; $a = 4.517 \text{ \AA}$ and $c = 3.020 \text{ \AA}$ for MgH₂ - Ellinger et al. [27]) regarding the 2:1 composites. On the contrary, a little cell expansion for both the compounds could be observed for the 1:2 composite. Concerning NaBH₄, this variation might be ascribed to the Mg incorporation in the interstitial vacancies of the complex hydride lattice, promoted by the mechanical treatment (Garroni et al. [28]). As for the microstructural parameters, the mechanical treatment allowed to reduce the crystallites size of MgH₂ down to



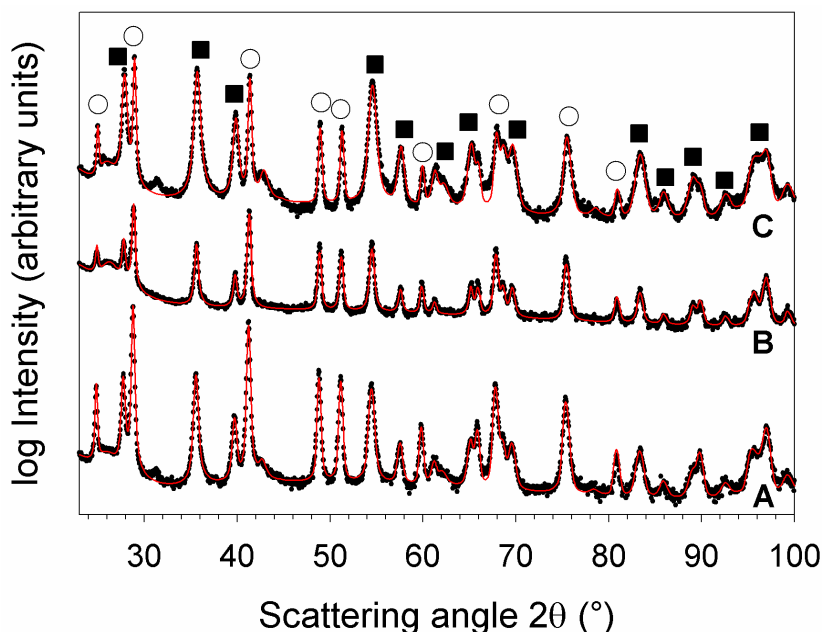


Figure 1: Experimental (black dotted profiles) and calculated (grey lines) XRPD patterns acquired on the samples: 2 NaBH₄:1 MgH₂ milled under Ar at 1050 rpm (A); 2 NaBH₄:1 MgH₂ milled under H₂ at 1050 rpm (B); NaBH₄:2 MgH₂ milled under Ar at 875 rpm (C). ○: NaBH₄; ■: MgH₂.

Table 1: Crystallites average size, lattice disorder and lattice parameters of the two hydrides in the different composites as obtained by the Rietveld refinement method.

NaBH ₄ : MgH ₂	Phases (wt%)	Crystallites size (Å)	Lattice disorder / 10 ³	Lattice parameter (Å)
2:1 Ar - 1050 rpm	NaBH ₄ 76 MgH ₂ 24	720 350	1.8 2.3	a = 6.166 a = 4.518; c = 3.021
2:1 H ₂ - 1050 rpm	NaBH ₄ 75 MgH ₂ 25	460 320	1.0 0.7	a = 6.166 a = 4.519; c = 3.021
1 2 Ar - 875 rpm	NaBH ₄ 47 MgH ₂ 53	715 270	1.6 2.4	a = 6.172 a = 4.524; c = 3.024

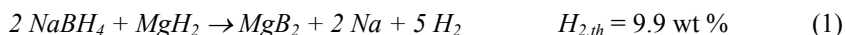
around 30 nm in all the samples. Conversely, milling seemed less effective in refining the microstructure of the complex hydride: an average size of about 46 nm was approached only when milling was carried out under H₂ and at the highest intensity.

The microstrain induced in the lattice was similar in the samples with different compositions milled under Ar but higher than that observed in the sample treated under hydrogen. It may be argued that the milling atmosphere

plays a key role in determining the microstructural characteristics of the H_2 active phases, and under H_2 atmosphere the mechanical action privileged the size refinement.

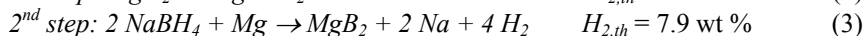
The morphology and the dimensions of the as-milled powders can be observed in Figure 2, where low magnification SEM micrographs are shown together with the related particle size distribution curves. Concerning the 2:1 composites, the average size of the powders agglomerates obtained by milling under H_2 is much smaller than the value obtained for the sample milled in Ar (about 66 μm vs. 116 μm , compare the distribution curves A and B). Agglomerates with an almost regular spherical shape can be found in both the composites (observe the smallest particles for the sample milled under Ar). Comparing Figures 2A and 2C, it can be seen that milling in Ar mixtures with 1:2 stoichiometry leads to average particles size much lower than that obtained for the sample with 2:1 composition (from the distribution curves average values of 23 μm and 116 μm are obtained), even if the former were processed at rotation rate lower than the latter. This observation suggests that the MgH_2 powders are more fragile and brittle than those of the borohydride, in agreement with the literature findings (Varin and Chiu [29]).

The measurements performed by the Sievert type apparatus showed that, independently on the processing atmosphere, the mixtures with composition 2 $NaBH_4$:1 MgH_2 release about 9.4 wt % H_2 . This value is close to the theoretical H_2 amount $H_{2,th}$ calculable for the full desorption of both the hydrides according to the reaction:



It is to note that the sorption processes are almost fully reversible, in the experimental conditions of this work, in the frame of one desorption/absorption/desorption cycle. Work is in progress to assess the reversibility of the processes upon several charging/discharging cycles at high temperature.

Thermal programmed desorption measurements allow to separate the dehydrogenation steps in order to study their onset temperatures and to evaluate their kinetics. The profile acquired for the sample milled in H_2 is reported in Figure 3. Two steps can be clearly distinguished during desorption. On the basis of the experimental H_2 amount released in each step (2.0 wt % H_2 and 7.5 wt % H_2 respectively), the following mechanism can be hypothesized:



MgH_2 dehydrogenation starts at 380 $^{\circ}C$, while the $NaBH_4$ dissociation takes place during the isothermal stage at 450 $^{\circ}C$, in agreement with the data recently reported by Garroni et al. [28]. The average rates of the two processes are $5.60 \cdot 10^{-2}$ wt % H_2 /min and $1.5 \cdot 10^{-2}$ wt % H_2 /min respectively. For the sample milled under Ar, the two processes takes place at lower temperatures (they begin at 315 $^{\circ}C$ and 390 $^{\circ}C$ respectively) but their average rate is consistently lower ($3.30 \cdot 10^{-2}$ wt % H_2 /min and $0.9 \cdot 10^{-2}$ wt % H_2 /min).

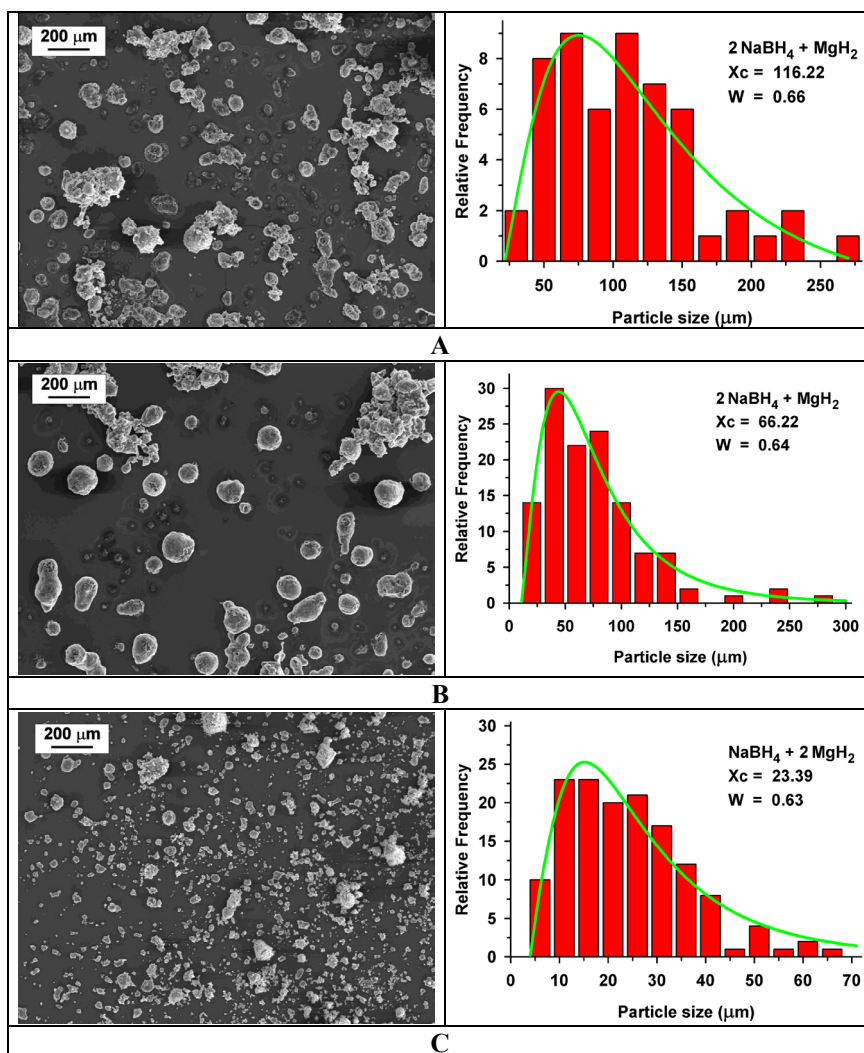


Figure 2: SEM images (50X) and granulometric distribution curves acquired on samples: $2\text{NaBH}_4\text{:}1\text{MgH}_2$ milled under Ar at 1050 rpm (A); $2\text{NaBH}_4\text{:MgH}_2$ milled under H_2 at 1050 rpm (B); $\text{NaBH}_4\text{:}2\text{MgH}_2$ milled under Ar at 875 rpm (C). X_c = average particles size (μm); W = average width of the distribution.

This means that milling under reactive atmosphere improves the kinetic performance of the composites.

The desorption profile of the $\text{NaBH}_4\text{:}2\text{MgH}_2$ mixture milled under Ar is reported in Figure 4. Also in this case, the first step can be attributable to the dissociation of MgH_2 (the amount of H_2 released in this step is perfectly

coincident with $H_{2,th} = 4.5$ wt %) and the second step to the reaction between the newly formed Mg and $NaBH_4$ (the experimental amount of released H_2 is 4.0 wt % to be compared with a theoretical value of 4.5% for full $NaBH_4$ dehydrogenation). The MgH_2 desorption starts at a temperature a little higher than that of the 1:2 sample milled under Ar (335 °C vs. 315 °C) but shows a noticeably higher rate (22 wt % H_2 /min vs. 3.3 wt % H_2 /min). On the contrary, the $NaBH_4$ dissociation takes place in the two mixtures with identical starting temperature and similar average rate (1.2 wt % H_2 /min vs. 0.9 wt % H_2 /min). The above consideration confirms the fact, already noticed in literature (Johnson et al. [30], Czujko et al. [21]), that $NaBH_4$ is a good catalyst towards the Mg/MgH_2 system.

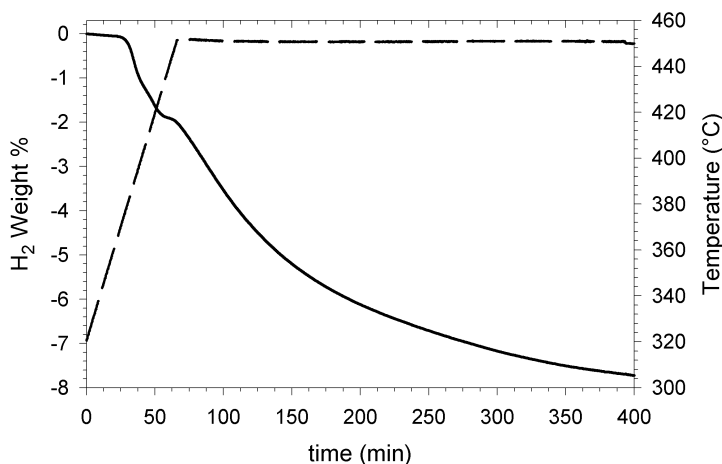


Figure 3: Desorption profile acquired on $2NaBH_4:1MgH_2$ mixture after milling under H_2 . To make the first step (MgH_2 dissociation) more evident, only the initial quicker part of the second step ($NaBH_4$ dissociation) was reported.

From the TPD results it can be concluded that the presence of MgH_2 , introducing a new decomposition pathway for $NaBH_4$, leads to a destabilization of this hydride, as testified by the decrease of its decomposition temperature with respect to the pure phase (Stasinevich and Egorenko [7], Ostroff and Sanderson [8]). The effect seems stronger when milling is performed under Ar. On the contrary, the MgH_2 dehydrogenation takes place at even higher temperatures than those characterizing the pure phase (that decomposes at around 300 °C when the H_2 pressure is 1 bar, Sandia Laboratory Hydride Properties Database [31]). This behaviour was observed also for the $LiBH_4 - MgH_2$ RHC (Vajo et al. [15], Yu et al. [32]).

The high pressure differential scanning calorimetry measurements are as interesting. The desorption profiles acquired upon heating the samples at 3 °C/min in isobaric conditions is composed of three subsequent endothermic peaks. Work is in progress to correctly attribute these peaks to the corresponding

dehydrogenation/decomposition reactions. No exothermic signal attributable to the formation of MgB_2 [expected on the basis of the desorption mechanism hypothesized in reactions (1)] is distinguishable: this could be ascribed to the fact that this reaction takes place contextually with the strongly endothermic dissociation of NaBH_4 [see reaction (3)]. The enthalpy value for the full dehydrogenation of both the 2:1 and the 1:2 system according to reaction (1), obtained by the integration of the whole calorimetric signal, is $72 \pm 2 \text{ kJ/mol H}_2$ (the values are the average of 3 measurements performed at constant H_2 pressure = 0.4 bar). The enthalpy values obtained for the dehydrogenation of MgH_2 and NaBH_4 are $76 \pm 2 \text{ kJ/mol H}_2$ and $86 \pm 2 \text{ kJ/mol H}_2$ respectively. This means that the dehydrogenation enthalpy of the here studied RHC is independent on the molar ratio between the constituent hydrides, it decreases by an amount of around 14 kJ/mol H_2 with respect to the individual compound NaBH_4 and it is almost the same as the pure MgH_2 phase. It is to note that, to the best of our knowledge, no experimental enthalpy values have been up to now reported concerning these RHC systems. A comparison with theoretical calculations indicates that the experimental desorption enthalpy here reported is 10 kJ/mol H_2 higher than the value expected for the 2:1 system (62 kJ/mol H_2 - NIST Chemistry Web Book [33]).

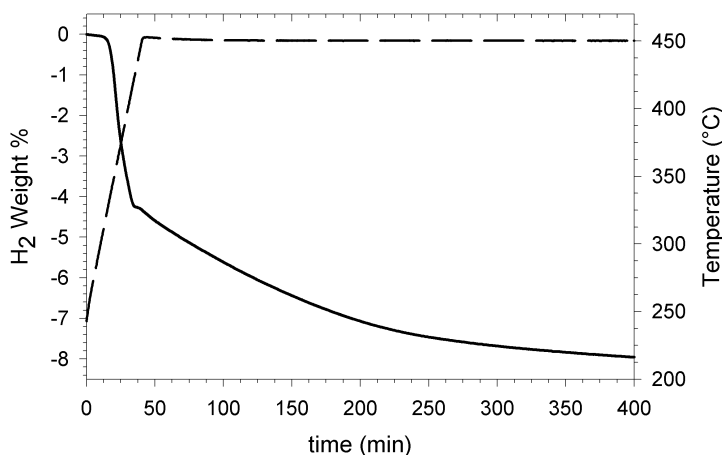


Figure 4: Desorption profile acquired on $\text{NaBH}_4\text{:}2\text{MgH}_2$ mixture after milling under Ar. To make the first step (MgH_2 dissociation) more evident, only the initial quicker part of the second step (NaBH_4 dissociation) was reported.

4 Conclusions

In this paper, some preliminary results obtained on the $\text{NaBH}_4 - \text{MgH}_2$ hydrogen storage system prepared by high energy ball milling are reported. The 2:1 and 1:2 composites were characterized concerning their structural and

microstructural characteristics and their storage performance as a function of the milling atmosphere. From TPD measurements performed in a Sievert type apparatus it can be hypothesized that, irrespective of the mixtures stoichiometry, the desorption process takes place in two steps, namely the MgH_2 dehydrogenation and the subsequent NaBH_4 decomposition, driven by the presence of the just formed Mg, to give MgB_2 , NaH and H_2 . The opening of this new decomposition route results in the complex hydride NaBH_4 destabilization, as evidenced by the decrease of its desorption temperature and enthalpy with respect to the pure phase, while the properties of the light hydride MgH_2 are not significantly modified. All the mixtures release an overall H_2 content close to the theoretical value calculable on the basis of the above quoted mechanism. Due to the higher amount of the more brittle component MgH_2 , the 1:2 mixture shows the smallest average grain size, and hence the best desorption kinetics. The sorption processes are reversible, in the frame of a discharging/recharging/discharging cycle. Unfortunately, both the working temperatures of the mixtures and the sorption kinetics (the rate limiting process being the NaBH_4 dissociation) are not yet suitable for on-board applications. Work is in progress to find suitable catalyzing/destabilizing agents able to both reduce the desorption temperature of the systems and to improve the kinetic properties of the NaBH_4 sorption reactions.

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