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# Microstructural study of hydrogen desorption in $2NaBH_4 + MgH_2$ reactive hydride composite

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ABSTRACT

The desorption mechanism of as-milled $2NaBH_4 + MgH_2$ was investigated by volumetric analysis, X-ray diffraction and electron microscopy. Hydrogen desorption was carried out in 0.1 bar hydrogen pressure from room temperature up to 450 °C at a heating rate of 3 °C $min^{-1}$. Complete dehydrogenation was achieved in two steps releasing 7.84 wt.% hydrogen. Desorption reaction in this system is kinetically restricted and limited by the growth of $MgB_2$ at the $Mg/Na_2B_{12}H_{12}$ interface where the intermediate product phases form a barrier to diffusion. During desorption, $MgB_2$ particles are observed to grow as plates around NaH particles.



## 1. Introduction

Solid state chemical storage of hydrogen in metals offers promising advantages over compressed hydrogen gas and condensed liquid hydrogen, especially for mobile applications with respect to safety and energy efficiency. However, no single metal hydride simultaneously satisfies the essential performance criteria for onboard hydrogen storage [1,2].

A breakthrough achievement was made by the development of reactive hydride composites [3,4] in which two metal hydride systems (e.g. $NaBH_4$ and $MgH_2$) are mixed together resulting in better sorption properties than those of individual pure systems.

The reactive hydride composite of $2NaBH_4 + MgH_2$ with a high theoretical hydrogen capacity of 7.8 wt.% offers considerable promise in this regard. However, kinetics and thermodynamics of absorption and desorption reactions remain key issues in hydrogen storage materials for mobile applications [5–8]. Thermodynamically, this composite system has an overall reaction enthalpy of 62 kJ $mol^{-1}$ $H_2$ resulting in an equilibrium temperature of 350 °C in 1 bar hydrogen pressure. But, recent experimental analysis [9] has shown some variation in properties. Earlier studies [10] revealed a two-step dehydrogenation process and the possibility of decreasing the sorption temperature by varying the stoichiometric ratio of the composite. Similar studies [11,12] showed a multi step desorption process starting at 320 °C, involving the desorption of $MgH_2$ to Mg, disproportionation of $NaBH_4$ through an intermediate stage to finally form $MgB_2$ and NaH.

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Electron microscopy is an essential tool for analysing and understanding the relationship between structure, morphology and the limiting reactions associated with complex metal hydrides. The high sensitivity of metal hydrides to air and moisture makes it difficult to prepare samples for Transmission Electron Microscopy (TEM) investigation. However, electron microscopy studies have been successfully carried out on binary and complex metal hydrides systems [13–17].

In this work the mechanism and pathway of the reaction $2NaBH_4 + MgH_2 \leftrightarrow 2NaH + MgB_2 + 4H_2$ were analysed using multiple experimental techniques like volumetric measurements, X-ray diffraction and especially Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

## 2. Experimental

Commercially available $NaBH_4$ and $MgH_2$ (98% purity) powders were purchased from Alfa–Aesar. Nanostructured samples of $2NaBH_4 + MgH_2$ were prepared by ball milling in an SPEX 8000 mill for 1 h with a ball to powder weight ratio of 10:1. Hydrogen desorption measurements were performed by thermo-volumetric titration in 0.1 bar hydrogen pressure, using a C2-3000 Sievert's-type apparatus designed by Hera Hydrogen Systems, Quebec, Canada. The samples were heated from room temperature up to 450 °C at a heating rate of 3 °C/min, and then held isothermally at this temperature for several hours. X-ray powder diffraction analysis was carried out using a Siemens D5000 diffractometer with Cu K$\alpha$ radiation ($\lambda$ = 0.15406 nm). SEM investigations were carried out using a ZEISS DSM 962 scanning electron microscope.

Material handling, milling and sample preparation for SEM and TEM were done in a dedicated glove box under a continuously purified argon atmosphere because of the high sensitivity of these hydride materials to air and moisture.

For TEM, a ground powder sample was dispersed in n-hexane and a drop of the supernatant liquid placed on a lacey-carbon film supported on a copper grid. The solvent was first evaporated off under vacuum in the microscope airlock after which the sample was inserted into the microscope.

TEM and high resolution TEM (HRTEM) investigation were carried out using the JEOL-JEM-3000F field emission gun (FEG) microscope operating at 300 kV with a point resolution of 0.16 nm. A double tilt specimen holder with +/−25° tilt capability was used. The microscope is also equipped with a Fischione high angle annular dark field (HAADF) detector, Gatan imaging filter (GIF), 2 k 794IF/20 Mega scan CCD camera – which allows chemical analysis using electron energy loss spectroscopy (EELS) and an Oxford Instruments energy dispersive X-ray (EDX) spectrometer.

## 3. Results and discussion

Fig. 1a shows an SEM image of the as-milled $2NaBH_4 + MgH_2$ system. The particle size distribution of the material appears to be divided in two main domain sizes. In particular it is possible to observe a portion of material having a particle size of 5–10 μm and another part constituted of much larger particle diameters of 20–30 μm. In spite of several attempts to identify the component phases through the SEM-EDX technique, no clear results were obtained. Considering that in the system, $2NaBH_4 + MgH_2$ the $NaBH_4$ volume fraction is roughly 80% of the total volume, it is reasonable to assume that the two compounds are well-mixed and $MgH_2$ particles are mostly surrounded by the $NaBH_4$.

The XRD analysis of the as-milled material ($2NaBH_4 + MgH_2$) in Fig. 1b shows the presence of $NaBH_4$, $\beta$–$MgH_2$ and a small amount of $\gamma$–$MgH_2$. The presence of the $\gamma$–$MgH_2$ is due to the high mechanical attrition generated during the ball milling, which partially converted the starting $\beta$–$MgH_2$ into the high-pressure polymorph $\gamma$–$MgH_2$ [18]. From Rietveld analysis of the diffraction pattern presented in Fig. 1b, it is possible to attribute to the $NaBH_4$ and the $\beta$–$MgH_2$ a crystallite size of 95 nm and 17 nm respectively.

Fig. 2 shows the bright field and high resolution (HRTEM) images of as-milled $2NaBH_4 + MgH_2$ with the selected area electron diffraction (SAED) pattern as inset in Fig. 2a. Both images show $NaBH_4$ and $MgH_2$ as major phases in the system after milling. The bright field image shows a nanosized distribution of $NaBH_4$ and $MgH_2$ grains inside the polycrystalline powder as indicated by uniform diffraction rings in the SAED pattern. The indexed SAED pattern indicates strong intensities from cubic $NaBH_4$ and tetragonal $MgH_2$ phases and shows good stability under the electron beam with no

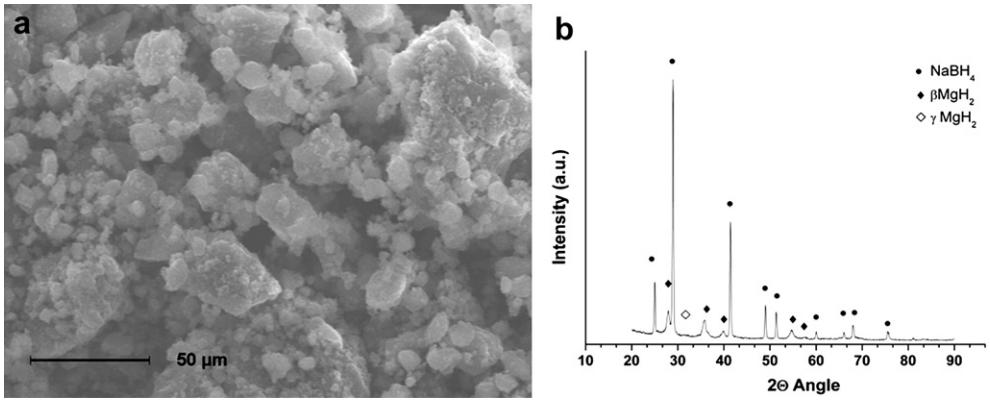


**Fig. 1 – (a) SEM image of as-milled $2NaBH_4 + MgH_2$ system (b) X-ray powder diffraction pattern of as-milled $2NaBH_4 + MgH_2$ composite.**