

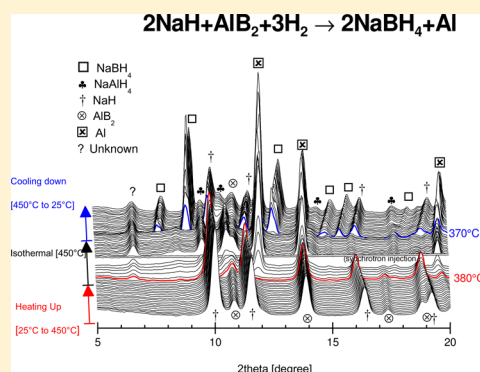
On the Hydrogenation of a NaH/AlB₂ Mixture

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ABSTRACT: A mixture of 3NaH/AlB₂ was prepared by ball-milling; its hydriding reaction was studied between 375–425 °C and 25–50 bar hydrogen pressure by means of volumetric titration. The hydriding reaction was characterized by means of in situ synchrotron radiation powder X-ray diffraction and high-pressure differential scanning calorimetry. Hydriding reaction took place at the molten state, and its reaction products were NaBH₄ and Al. The scanning electron microscopy images of the material revealed that the material morphology changes after hydriding. A maximum hydrogen uptake of 4.7 wt % was registered for the hydriding experiment at 425 °C and 50 bar hydrogen pressure. Dehydriding reaction was studied by means of volumetric titration and differential scanning calorimetry. The dehydriding reaction at 425 °C and 1 bar argon pressure registered a release of 2.4 wt %. The low dehydriding level was attributed to the reduction of the available particle surface upon melting of the material during the hydriding reaction.



1. INTRODUCTION

Hydrogen storage in the solid state is one challenging factor for the successful development and commercialization of fuel cell applications, either mobile or stationary. Today, no single hydrogen storage material fulfills all requirements on capacity, operational pressures and temperatures, reaction kinetics, reaction enthalpy, and cost necessary for practical applications. Ingenious mixing of materials seems promising in adjusting favorably some of those requirements. The mixtures or composites of metal borohydrides and metal hydrides are promising materials due to the possibility to lower the dehydrogenation enthalpy,^{1,2} changing the reaction pathway of individual components, or surpassing kinetic constraints.^{3,4} The reactive hydride composite: $2\text{NaBH}_4 + \text{MgH}_2 \leftrightarrow 2\text{NaH} + \text{MgB}_2 + 4\text{H}_2$ (hereafter Na-RHC) has been profusely investigated:⁵ prepared as $2\text{NaBH}_4 + \text{MgH}_2$ and studying the dehydriding reaction,⁶ or prepared as $2\text{NaH} + \text{MgB}_2$ and studying the hydriding reaction,⁷ where the side formation of NaMgH_3 has been observed. The formation of NaMgH_3 at the Na-RHC, that can account for as much as 18 wt %, ⁸ is not desirable due to the lowering in the hydrogen uptake. However, NaMgH_3 by itself can be considered a hydrogen storage material,⁹ but its high thermodynamic stability¹⁰ and thus its high decomposition temperature¹¹ prevent its use. In short, when Na, Mg, and H are present in a hydrogen storage system, NaMgH_3 is expected to be formed.¹²

AlB₂ and MgB₂ share the same crystal structure (P6/mmm space group); up to now, AlB₂ has been used as a modifier of the superconducting properties of MgB₂.¹³ Surprisingly, regardless of the large amount of boron-based hydrogen storage materials,¹⁴ just a few theoretical¹⁵ or experimental

examples can be found on the use of AlB₂ as a boron source: $2\text{LiBH}_4 + \text{Al} \leftrightarrow \text{AlB}_2 + 2\text{LiH} + 3\text{H}_2$ ^{16–18} or $\text{CaH}_2 + \text{AlB}_2 + 3\text{H}_2 \rightarrow \text{Ca}(\text{BH}_4)_2 + \text{Al}$.¹⁹ To the best of our knowledge, hydrogenation of NaH/AlB₂ has been not reported. In the present work, we propose the use of AlB₂ as the source of boron instead of MgB₂ and the study of a new material that can be classified as a reactive hydride composite. The possible hydrogenation products of the NaH/AlB₂ mixture were anticipated as NaBH₄, NaAlH₄, or a mixture of them plus Al; covering these possibilities, the 3NaH + AlB₂ mixture was produced by ball-milling, hydrogenated, and characterized. For completeness, dehydriding reaction experiments were performed.

2. EXPERIMENTAL DETAILS

Raw materials NaH (95% purity) and AlB₂ (95% purity) were purchased from Sigma-Aldrich and used as received. The 3NaH + AlB₂ mixture was prepared by ball-milling in batches of 1 g as necessary. The mill was an SPEX 8000. The milling vial was made of hardened steel with an internal volume of 200 mL. Three balls of 1 cm in diameter made of ceramic zirconium were used. No process agent control was used. The ball-to-powder ratio was 10:1. The milling time was 6 h in 4 cycles of 90 min of milling and 15 min resting. All powder handling, sealing of the milling vial, and milling were carried out in an

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argon-filled glovebox. The concentrations of H₂O and O₂ were below 10 ppm in the glovebox.

Hydrogen sorption experiments were carried out in a PCTPro-2000 from Hy-Energy instrument or in a carefully calibrated Sievert's type apparatus (HERA, Quebec, Canada). Two operation modes were used. In the first operation mode, the samples were fast heated to 375 °C under 1 bar argon atmosphere. At the isothermal condition, the H₂ pressure was adjusted to 25 or 50 bar. In the second operation mode, a fresh sample at room temperature was settled to 50 bar hydrogen pressure; then, the sample was heated to 425 °C at a 1 °C/min heating rate. While this work is dedicated to the hydriding properties of the 3NaH/AlB₂ mixture; for completeness, a sample of previously hydrogenated material (at 50 bar and 425 °C) was heated to 425 °C at a 2.5 °C/min heating rate under 1 bar argon atmosphere.

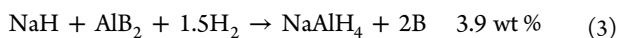
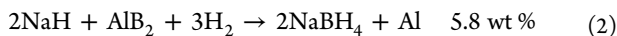
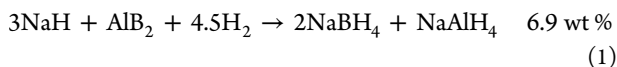
The hydrogenation reaction was followed by means of in situ synchrotron radiation powder X-ray diffraction (SR-PXD). The experiments were performed at the D3 beamline at DORIS at Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany. The samples were confined in sapphire capillaries without oxygen contact. In turn, the sapphire capillaries were mounted in a dedicated X-ray diffraction cell for solid–gas reactions²⁰ and fixed in front of the beam trajectory. Then, the hydrogen pressure was settled to 25 or 50 bar; the samples were heated at a 5 °C/min heating rate until 450 °C. After 1 h at the isothermal condition, the samples were allowed to cool down to room temperature. The wavelength was 0.50003 Å. The two-dimensional powder diffraction images were taken at 10 s exposure time plus suitable reading and clearance time of the CCD detector. Two-dimensional powder diffraction data were integrated by the Fit2D program.²¹ PXD peak assignment was performed with the MAUD software.²² Crystallographic information for phase identification was taken from the Inorganic Crystal Structure Database (ICSD).

High-pressure differential scanning calorimetry (HP-DSC) experiments were performed at 25 and 50 bar constant hydrogen pressure. The measurements were performed at a heating rate of 5 °C/min. An HP-DSC Netzsch equipment was used. Additionally, a previously hydrogenated material (at 50 bar and 425 °C) was characterized by DSC using a Netzsch STA 409 equipment. The sample was heated from room temperature to 500 °C with a heating rate of 5 °C min⁻¹ under an argon flow of 50 mL min⁻¹.

Scanning electron microscopy (SEM) images were taken in as-milled material and at a hydrogenated material (50 bar and 425 °C). Sample imaging were taken in a JEOL7600F microscope with an acceleration voltage of 10 kV, or in a Leica Stereoscan 440 microscope with an acceleration voltage of 20 kV.

3. RESULTS AND DISCUSSION

3.1. Thermodynamic Considerations of the Hydriding of the 3NaH/AlB₂ Mixture. First, it must be established what to expect of the hydrogenation of the 3NaH/AlB₂ mixture. The three possible reactions and products of the mixture were proposed as



At the hydrogenation of NaH/MgB₂ (Na-RHC), the formation of MgH₂ (along with NaBH₄) is well-documented.⁷ At the hydrogenation of NaH/AlB₂, the formation of AlH₃ is out of the picture unless, in future work very high-pressure,²³ a suitable stabilizer, a dopant, or a catalyst might be used. Taking into account the excess of NaH in reactions 2 and 3, the maximum hydrogen uptake expected at the 3NaH/AlB₂ mixture is 4.7 and 2.4 wt %, respectively. Elemental boron is considered as chemically rather inert. The reported values for the standard formation enthalpy of AlB₂ range from -151.00 to -23.01 kJ/mol.²⁴ The most accepted value, and used here, is -66.9 kJ/mol.^{24,25} The standard formation enthalpies of NaH, NaBH₄, and NaAlB₄ were taken as -45.5,²⁶ -245.5,²⁶ and -117.0 kJ/mol,²⁷ respectively. The reaction enthalpies of the depicted reactions are thus: reaction 1, -404.5 kJ/mol; reaction 2, -333.0 kJ/mol; and reaction 3, -4.6 kJ/mol. The hydrogenation reaction is expected to occur according to reactions 1 and 2; meanwhile, the dehydrogenation reaction is expected to be difficult.

3.2. Kinetics of the Hydriding of the 3NaH/AlB₂ Mixture. Figure 1 presents the sorption experiments in the

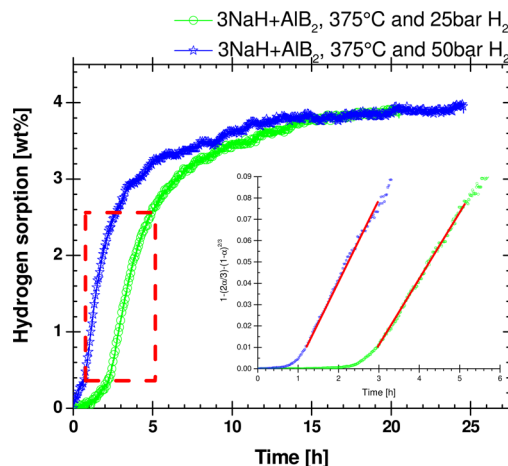


Figure 1. Hydriding reaction of the 3NaH/AlB₂ mixture at 375 °C and 25 or 50 bar hydrogen pressure. Inset: kinetic modeling of the reaction.

first operation mode, i.e., heating up to 375 °C and then adjusting the initial hydrogen pressure to 25 or 50 bar. The hydriding reaction is slower for the 25 bar experiment than for the 50 bar experiment because of the higher driving force. In both experiments, three regions can be observed:

- (1) A region of small hydrogen uptake at the beginning of the experiment. This region appears to be pressure-dependent. At 25 bar, it had a duration of about 2.5 h; meanwhile, at 50 bar, it had a duration of about 1 h. This region is possibly related to nucleation of the hydride phases.
- (2) The second region corresponds to fast hydrogen uptake. This region traditionally has been described by a two-dimensional or a three-dimensional growth of existing nuclei, with constant or decreasing interface velocity, i.e., the Johnson–Mehl–Avrami equation or posterior modifications.^{28,29} In the present work, data were best described by the contracting volume, three-dimensional growth diffusion controlled model with decreasing interface velocity³⁰

$$1 - \left(\frac{2\alpha}{3}\right) - (1 - \alpha)^{2/3} = kt \quad (4)$$

where α is the transformed fraction, i.e., the ratio between the hydrogen uptake at a time t and the maximum of the hydrogen uptake, and k is the velocity constant. The inset of Figure 1 presents the application of the model eq 4. The left side of eq 4 is presented at the ordinate. The abscissa is the time t , and k was obtained from the slope. The red line in each curve indicates the fitting section for the second region. The red dashed square indicates the fitting section in the initial kinetic data. The estimated k values are $k = 8.56 \times 10^{-6} \text{ s}^{-1}$ for the experiment at 25 bar ($R^2 = 0.995$, at 3–5 h), and $k = 1.01 \times 10^{-5} \text{ s}^{-1}$ for the experiment at 50 bar ($R^2 = 0.996$, at 1–3 h). The k values are pressure-dependent.

- (3) The third region presented slow hydrogen uptake near its maximum, and it is located at a long experimental time, i.e., after 5 h of hydrogen exposure, and was not modeled. At both experiments, 25 and 50 bar, the maximum amount of hydrogen uptake was 3.9 wt %.

Figure 2 presents the absorption experiment at the second operation mode, i.e., initial setting of the pressure and then the

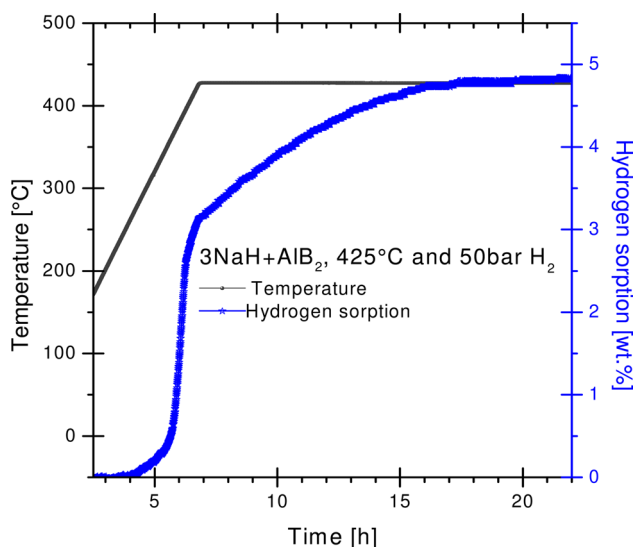


Figure 2. Hydriding reaction of the 3NaH/AlB₂ mixture at 425 °C. Heating rate of 1 °C/min and 50 bar hydrogen pressure.

heating up. The increase of hydriding temperature from 375 °C (Figure 1) to 425 °C leads to an increase of the final hydrogen uptake from 3.9 to 4.7 wt %, in agreement with the proposed reaction 2. The hydriding reaction started slowly about 270 °C; then, a fast hydrogen uptake took place at 370 °C. This fast hydrogen uptake lasted until the system reached 425 °C, when the hydriding reaction slowed down until reaching the final 4.7 wt %.

3.3. Hydriding Pathway of the 3NaH/AlB₂ Mixture. To confirm the hydriding pathway of the 3NaH/AlB₂ mixture, in situ SR-PXD and HP-DSC were performed. Main phases involved at the hydriding pathway were identified as AlB₂, 43851-ICSD, *P6/mmm*; NaH, 33670-ICSD, *Fm3m*; NaBH₄, 419039-ICSD, *Fm3m*; and Al, 43423-ICSD, *Fm3m*. Figure 3 presents the in situ SR-PXD characterizing the hydriding reaction of the 3NaH/AlB₂ mixture at 50 bar hydrogen

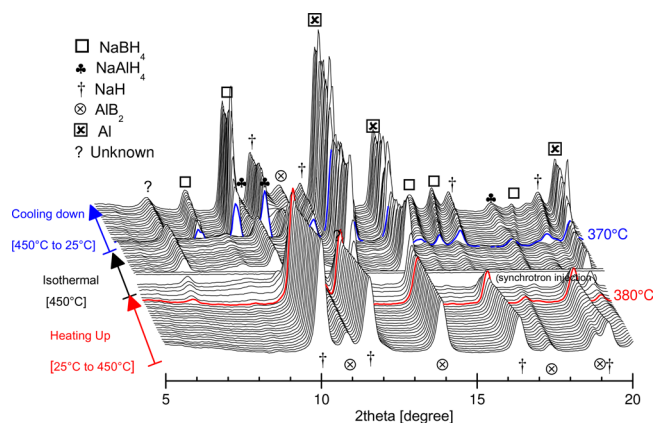


Figure 3. In situ SR-PXD hydriding reaction of the 3NaH/AlB₂ mixture at 425 °C and 50 bar hydrogen pressure. Heating rate: 5 °C/min. D3 beamline, DESY.

pressure. The experiment progression is presented from front to back of Figure 3. In the beginning, just the NaH and AlB₂ peaks were present. At about 380 °C, the NaH peaks showed a small increase, quickly followed by complete vanishing due to melting. NaH is reported to melt (and decompose) at 426 °C.²⁷ In the related NaH/MgB₂ system, the NaH peaks' disappearance was observed to occur at 330 °C.⁷ The decrease of the NaH melting point is consistent with the NaH mixing with AlB₂ or MgB₂. Immediately after the NaH-peaks vanished, the emerging of Al peaks along with three unidentified peaks at 5.5, 9.5, and 10.5° in 2θ were observed. An unexpected synchrotron injection was caught during the isothermal period of the experiment, but no crucial information was lost. During the complete isothermal period at 450 °C, the Al peaks displayed a notable increase in intensity. The unknown peaks presented a small intensity increase; meanwhile, the AlB₂ peaks' intensities were slowly decreasing. No hydrogenated products were evident until reaching 370 °C during cooling down. At this point, the NaBH₄ and NaH peaks emerged suddenly, with the NaBH₄ peaks growing until the end of the experiment. A minor NaAlH₄ (655434-ICSD, *I41/aS*) formation was observed to evolve during cooling down. NaAlH₄ main peaks evolved from the unidentified 9.5° and 10.5° peaks in 2θ observed initially at isothermal conditions. The peak at 5.5° in 2θ remained unidentified.

Figure 4 presents the in situ SR-PXD characterizing of the hydriding of the 3NaH/AlB₂ mixture at 25 bar. The reaction pathway is quite similar to than at 50 bar. At the beginning (front of Figure 4), just the NaH and the AlB₂ compounds were present. Heating up leads to the complete melting of NaH at 413 °C; this temperature is slightly superior compared to the 50 bar reaction. The isothermal period was characterized by the appearance and growing of Al peaks. Again, there was no evidence of the expected hydrogenated products at the isothermal period. In this experiment, the cooling down was fast performed, at approximately 50 °C min⁻¹; thus, the emerging of NaBH₄ and NaH peaks was suddenly observed. No evidence of NaAlH₄ formation was obtained. The NaAlH₄ formation is well-recognized to be pressure-dependent,³¹ with a 100 bar hydriding pressure as the preferred value.³² Further explorations on the 3NaH/AlB₂ hydride kinetics and pathway must be performed at 100 bar and even higher pressures. For now, it can be established that, at the experimental conditions

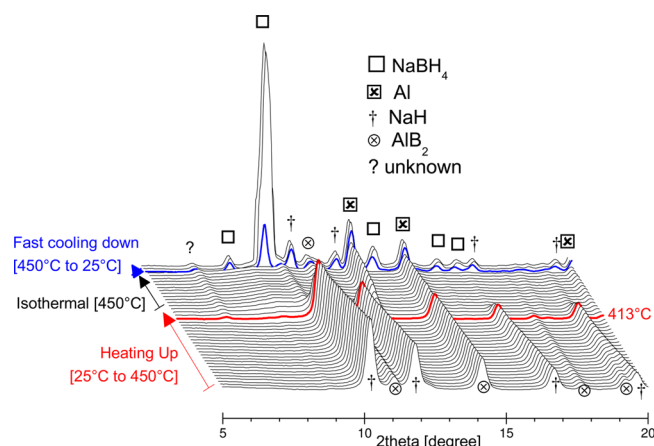


Figure 4. In situ SR-PXD hydriding reaction of the 3NaH/AlB₂ mixture at 425 °C and 25 bar hydrogen pressure. Heating rate: 5 °C min⁻¹. D3 beamline, DESY.

of 375–450 °C and 25–50 bar, the proposed [reaction 2](#) took place.

[Figure 5](#) presents the HP-DSC traces of hydriding reactions of the 3NaH/AlB₂ mixture at 25 and 50 bar. The reaction is

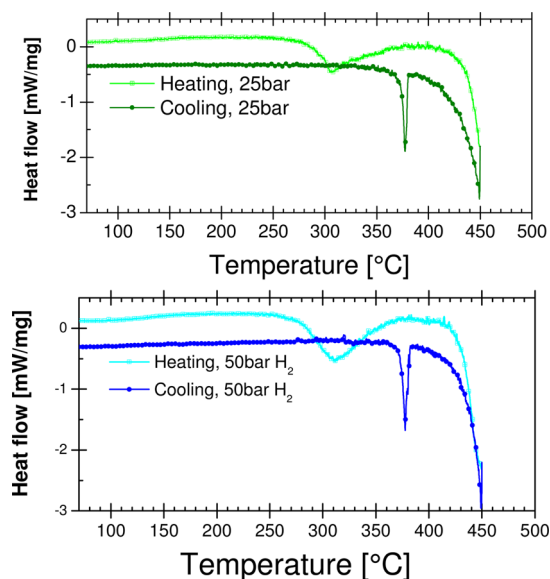


Figure 5. HP-DSC traces of hydriding reaction of the 3NaH/AlB₂ mixture at 25 and 50 bar hydrogen pressure. Heating rate: 5 °C/min.

similar at both hydriding pressures. During the heating, one exothermic peak with an onset at 270 °C was observed. This is coincident with the beginning of the hydride reaction observed in [Figure 2](#). The end of the heating up was marked by an exothermic peak with an onset at 380 °C, in agreement with the NaH peaks disappearing observed in [Figures 3](#) and [4](#). The cooling down period was marked by a sharp peak at 377 °C that can be associated with the sudden solidification of NaBH₄ and NaH. This solidification also was observed in [Figures 3](#) and [4](#). From in situ SR-PXD and HP-DSC experiments, it can be determined that the hydriding [reaction 2](#) takes place in a molten state. The events of the hydriding reaction of 3NaH/AlB₂ at 25–50 bar can be summarized as follows: (a) slow nucleation starting at 270 °C, (b) melting of NaH starting at 380°, (c) between 425 and 450 °C, developing of Al from AlB₂,

change of B-bonding, and formation of NaBH₄ in a molten state, and (d) crystallization of NaBH₄ at 377 °C during cooling.

3.4. Dehydriding of the Hydrided 3NaH/AlB₂ Mixture.

[Figure 6](#) presents the dehydriding reaction of a previously

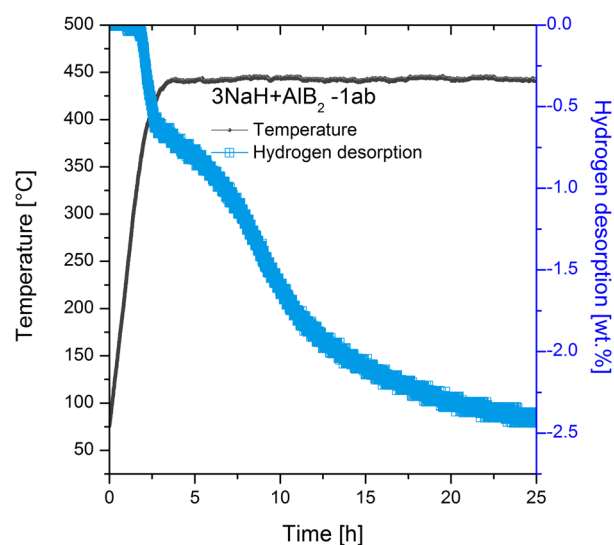


Figure 6. Dehydriding reaction of the 3NaH/AlB₂-1ab mixture at 425 °C. Heating rate of 2.5 °C/min and 1 bar argon pressure.

hydrided sample of 3NaH/AlB₂, hereafter 3NaH/AlB₂-1ab. The reaction did not start until reaching 360 °C; then, the reaction accelerated until reaching 415 °C. At this point, the reaction experienced another change in speed; it was slowed down. An additional slowing down was observed around the 7th hour of reaction. The reaction is clearly multistep. However, the desorbed hydrogen was only 2.4 wt %; this amount is practically half of the previously stored hydrogen.

To help in understanding the dehydriding reaction, DSC of the 3NaH/AlB₂-1ab sample was collected. [Figure 7](#) presents the

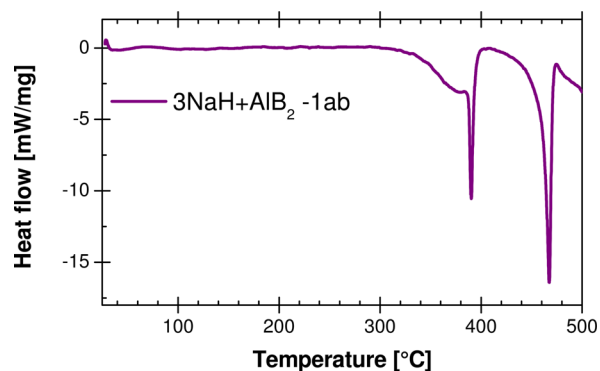


Figure 7. DSC trace of dehydriding reaction of the 3NaH/AlB₂-1ab mixture at 425 °C. Heating rate of 5 °C/min and argon flow of 50 mL/min.

DSC trace. A broad peak with an onset at 340 °C and two sharp peaks at 390 and 467 °C were observed. The broad peak can be related to the beginning of the dehydriding reaction, as observed at [Figure 6](#). The peak at 390 °C is related to the melting of the excess of NaH remaining in the reacting mixture. The peak at 467 °C is related to the decomposition of NaBH₄.

The DSC tracing is in agreement with the multistep dehydriding reaction observed in Figure 6.

The decomposition temperature of NaBH_4 has been reported between 534 and 565 °C.²⁶ The reduction of the NaBH_4 decomposition temperature is, in fact, one intended objective by the reactive hydride composite approach. Still, this temperature is too high for mobile fuel cell applications; stationary applications can still be viable if complete dehydriding reaction would succeed.

Figure 8a presents the SEM image of the as-milled 3NaH/ AlB_2 mixture. The image shows spherical particles of about 1

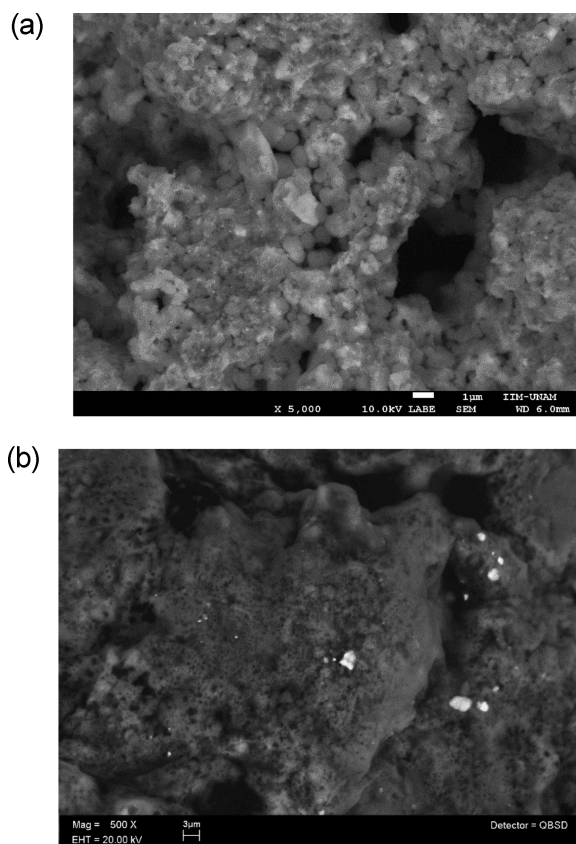


Figure 8. (a) SEM image of the as-milled 3NaH + AlB_2 mixture. (b) SEM image of the 3NaH + AlB_2 hydrided at 425 °C and 50 bar hydrogen pressure.

μm in diameter. These particles agglomerate in a three-dimensional-porous fashion. This kind of agglomeration is suitable for hydrogen storage, because hydrogen can reach the particle surface easily and then react. The result is the accomplishment of the complete hydrogen storage capacity of the proposed reaction 2, i.e., the 4.7 wt %, considering the excess of NaH.

Visual observation after hydriding reaction indicates that the material lost its powder previous morphology. After the hydriding reaction, the material got a porous solid structure. The hydrogenated material was only recovered by the use of sharp tools. Figure 8b shows the SEM image of the hydrided material at 50 bar hydrogen pressure and 425 °C. The material looks fused with no well-defined particle boundaries. Still, the material remained porous, allowing for partial hydrogen release.

As expected from the thermodynamic considerations, high dehydriding temperatures was observed. However, the incomplete hydrogen release can be explained by a severe

increase in particle size after melting during the hydriding reaction, i.e., a physical rather than a thermodynamic constrain.

4. CONCLUSIONS

The 3NaH/ AlB_2 mixture was produced by ball-milling and tested for hydrogen storage. Hydrogen absorption was studied in the temperature/pressure ranges of 375–425 °C and 25–50 bar hydrogen pressure. The hydrogenation of the 3NaH + AlB_2 composite led to NaBH_4 + Al formation with a maximum of 4.7 wt % of stored hydrogen. The kinetics rate was strongly dependent on the applied hydrogen pressure and temperature. Slow absorption with a delay time in the range of 1–2 h was observed below 380 °C, consistent with a nucleation step. At 425 °C, hydriding was performed through a molten state. The presence of NaBH_4 as the hydrogenation product was confirmed just after cooling down and crystallization of material. Herewith, AlB_2 was shown to act as a possible boron source for the formation of NaBH_4 in reactive hydride composite-type reactions. In this way, the formation of undesired hydrided byproducts was eliminated.

The dehydrogenation is found to be a multistep reaction starting at temperatures around 360 °C; however, the main NaBH_4 decomposition was observed at 467 °C. The dehydrogenation was found to be incomplete, which most likely can be attributed to a severe increase in particle size after melting.

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Notes

The authors declare no competing financial interest.

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