Title: Milling time effect of Reactive Hydride Composites of NaF-NaH-MgB$_2$ investigated by in situ powder diffraction

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Abstract

Light metal complex borohydrides have high hydrogen storage capacities but suffer from drawbacks of slow hydrogen sorption kinetics, poor reversibility and high thermodynamic stability. The NaF+9NaH+5MgB$_2$ composite has a theoretical hydrogen capacity of 7.7 wt% H assuming the formation of 10NaBH$_{3.9}$F$_{0.1}$+5MgH$_2$. Hydrogenation and dehydrogenation properties as well as the effect of different ball milling times have been investigated. The in situ hydrogenation is faster in the composite ball milled for 87 h than the 5 h milled composite. A boron-rich phase with space group $\text{Pa}-3$, $a = 7.4124(5)\ \text{Å}$ was formed during hydrogenation at 325 $^\circ$C and 50 bar hydrogen for both short and long milling times. In the long milled composite the boron-rich phase disappeared after 3 h of hydrogenation, whereas it became a major phase in the short milled composite after 1.5 h of hydrogenation. NaBH$_4$ was formed at 206 $^\circ$C. NaMgH$_{3-x}$F$_x$ was formed at 290 $^\circ$C instead of the assumed MgH$_2$. The same phases formed at 268 $^\circ$C and 325 $^\circ$C, respectively, and only in minor amounts in the short milled composite. Ex situ hydrogenation in a Sieverts' type apparatus at the same temperature and hydrogen pressure conditions followed a different reaction pathway with formation of MgH$_2$ in addition to NaBH$_4$ and NaMgH$_{3-x}$F$_x$ ($0 \leq x \leq 1$). The measured hydrogen uptake was 6.0 wt% and 6.3 wt% for the long and short milled composites, respectively.

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Introduction

Solid state hydrogen storage has the advantage over gaseous storage because of higher volumetric hydrogen storage capacities and lower pressures [1]. Reactive Hydride Composite (RHC) is an approach to tune the thermodynamics and kinetics of solid state hydrogen storage systems and make them more feasible for mobile application [2-4].

The stability of complex hydrides can be adjusted by anion substitution. Recently it was found that Na$_3$AlH$_{6-x}$F$_{x}$, formed from hydrogenation of NaF and Al, has a significant lower stability than Na$_3$AlH$_6$ [5, 6]. Substitution of hydrogen or a functional group with i.e. a halide, will change the bond strength, and the enthalpy of hydrogen sorption will be altered [7]. The hydrogenation properties of RHCs can thus be altered by partly substituting metal hydrides with metal halides i.e. fluorides, chlorides, bromides or iodides [8, 9].

It has been shown that a higher amount of hydrogen can be absorbed in CaH$_2$+MgB$_2$ when 25 mol% of the CaH$_2$ is substituted with CaF$_2$. The non-fluorinated system of CaH$_2$+MgB$_2$ has a theoretical hydrogen capacity of 8.3 wt%, but the experimental yield of absorbed hydrogen was only 3.5 wt%. The CaF$_2$-containing system absorbed twice as much hydrogen (7.0 wt%) with the same experimental conditions [10].

The theoretical hydrogen capacity of 2NaH+MgB$_2$ is 7.8 wt%, assuming that 2NaBH$_4$ and MgH$_2$ are formed under hydrogenation. It has been found that this reaction is plagued by slow hydrogen sorption kinetics and by a low experimental hydrogen absorption capacity of only 3.8 wt% [11-14]. Pistidda et al. investigated this system and observed the formation of a boron-rich phase with space group Pa-3 and a = 7.319 Å forming during hydrogenation [13]. The proposed composition is B$_{48}$, but the overall composition is still not clear, as the authors point out that inclusion in small amounts of other atoms like Mg and Na in the cubic lattice is possible [13].

This paper describes the adjustment of the thermodynamically stable 2NaH+MgB$_2$-system by substituting 10 mol% of the NaH with NaF forming NaF+9NaH+5MgB$_2$. Assuming a similar reaction pathway as above the theoretical hydrogen capacity would be 7.7 wt% for conversion for the starting reactions into 10NaBH$_{3.8}F_{0.1}$+5MgH$_2$. 
Experimental

Sample preparation: Commercially available powders of NaH (Sigma-Aldrich, >95%), MgB$_2$ (Sigma-Aldrich, >96%) and NaF (Sigma-Aldrich, >99%) were ball milled in a two-step process in a SPEX 8000D shaker mill for a total time of 87 and 5 h, respectively (long and short milled composite). The first step was to ball mill NaF-NaH in the molar ratio of 1:9 for about 60 h and 2.5 h, respectively. Then the products were ball milled with MgB$_2$ for 27 h and 2.5 h, respectively, in the molar ratio 2(NaF-NaH):1(MgB$_2$). Stainless steel vials with stainless steel-balls were used with a ball-to-powder ratio 10:1.

All sample manipulations were performed under argon atmosphere in a MBraun Unilab glove box with O$_2$/H$_2$O levels kept below 1 ppm.

Hydrogenation: Hydrogenations were performed in an in-house manufactured Sieverts-type apparatus. The sample was gently hand grinded with mortar and pestle prior to loading it in the Sieverts apparatus to reactivate after being stored in the glove box. The hydrogen absorption was carried out with a temperature ramp of 5 °C min$^{-1}$ from room temperature (RT) to 325 °C at 50 bar hydrogen pressure, followed by an isothermal step of 325 °C during a 41 h period.

Powder X-ray Diffraction (PXD): Data was collected using a Bruker AXS D8 Advance diffractometer in transmission mode, CuK$_{α}$ $λ = 1.5418$ Å, fitted with a Göbbel mirror and a LynxEye™ 1D strip detector. The samples were measured over the scattering angle (2θ) from 10 ° to 90 ° with a step size Δ2θ of 0.02 °. The samples were contained within rotating boron-glass capillaries with an inner diameter of 0.5 mm. They were sealed used a 0.3 mm diameter boron-glass stick and glue.

In situ - Synchrotron Radiation Powder X-ray Diffraction (SR-PXD) was conducted at the Swiss Norwegian Beam Lines, BM01A at ESRF in Grenoble, France [15]. Sapphire tubes (1.15 mm outer diameter, 0.8 mm inner diameter) connected to a Swagelok pressure cell were used. The high pressure gas rig and pressure cell are in-house manufactured. The in situ cycling experiments were conducted using a heating/cooling rate of 5 °C min$^{-1}$ from RT to 325 °C (hot air blower) with hydrogen pressure of 50 bar for absorption and 1 bar hydrogen backpressure for desorption (510 °C). A Pilatus 2M detector was deployed and the sample-to-detector distance was 246 mm at a wavelength of 0.80645 Å or 0.784624 Å, respectively. The exposure
times were 30 s giving a resolution of 2.5 °C per diffraction pattern. The cell was rotated by 10 ° during each exposure to improve powder averaging.

All obtained raw images were transformed to 1D-powder patterns using the FIT2D program [16]. The wavelength and sample-detector distance were calibrated from a LaB₆ standard. Single crystal reflections from the sapphire tube were masked out manually in Fit2D. The Rietveld refinements were performed with GSAS and Expgui software [17, 18]. The peak shapes were modeled with a Thompson-Cox-Hastings pseudo-Voigt function with four refineable parameters (three Gaussian and one Lorentzian) [19]. The backgrounds were fitted with a Chebyshev polynomial with up to 36 terms.

Results and discussion

Ball milled samples

Before the in situ hydrogenation, the samples were measured by SR-PXD in their “as-milled” state at RT. The width of the Bragg peaks is different after ball milling for 87 and 5 h, respectively (see Fig. S1 and S2 in Supporting information). In the long milled sample the Bragg peaks from the initial compounds NaH and NaF were replaced with broad peaks from a single fcc phase; FWHM = 0.228 ° at 2θ = 16.542 °. This corresponds to a particle size of 18 nm calculated using the Scherrer formula [20]. The lattice parameter of the face-centered cubic phase was a = 4.86529(8) Å. This lattice parameter is slightly smaller due to partial fluorine substitution (NaF a = 4.78 Å [21]) compared to that reported for NaH (a = 4.89 Å [22]). From Rietveld refinements the composition of this phase is proposed to be NaH₁₋ₓFₓ with x = 0.099(1), and thus confirming the formation of a single solid solution phase. In contrast, in the short milled sample, the Bragg peaks of F-substituted NaH and NaF were distinguishable after ball milling with FWHM = 0.128 ° for NaH at 2θ = 16.542 °, corresponding to a calculated particle size of 32 nm for NaH.

From Rietveld refinements with the SR-PXD data at RT for the 87 h milled sample (Fig. S1 in Supporting information), the fractions of the reactants were 44.5(2) wt% MgB₂, 51.2(3) wt% NaH₁₋ₓFₓ with x = 0.099(1) and 4.3(1) wt% Fe. Fe was a contamination from the ball mill. These values are in good agreement with the nominal composition, 47 wt% MgB₂, 44 wt% NaH and 8 wt% NaF (corresponding to 52 wt% NaH₀.₉F₀.₁).
The 5 h milled composite shows sharp Bragg peaks after ball milling, and all reactants can be identified (Fig. S2 in Supporting information). The refined phase composition was 37.0(6) wt% MgB$_2$, 59.6(6) wt% NaH$_{1-x}$F$_x$ with $x = 0.078(1)$ and 2.9(3) wt% for NaF. The incomplete incorporation of F$^{-}$ in the solid solution NaH$_{1-x}$F$_x$ is reflected in the smaller unit cell axis of $a = 4.8589(8)$ Å, compared 4.86529(8) Å in the 87 h milled sample. 0.5(1) wt% Fe is present as a contamination. The refined phase fractions are in agreement with the nominal composition.

**Hydrogenation of long milled NaF+9NaH+5MgB$_2$**

The *in situ* SR-PXD hydrogenation measurements were performed at 50 bar of H$_2$ heating the sample from RT to 325 °C with a heating rate of 5 °C min$^{-1}$ and followed by 5 h isotherm at 325 °C. The first hydrogenation product, NaBH$_4$, was observed at 206 °C (green curve in Fig. 1a). NaMgH$_{3-x}$F$_x$ started to form at 290 °C (red curve in Fig. 1a). This compound is more stable than MgH$_2$ and therefore the favored product [23, 24]. The intensity of the NaH$_{1-x}$F$_x$ Bragg peak at 16.5 ° was decreasing and becoming narrower when the NaMgH$_{3-x}$F$_x$ was formed, suggesting that fluorine from NaH$_{1-x}$F$_x$ was incorporated into NaMgH$_3$ structure. This was also evident from the increase of lattice parameters to $a = 5.47345(16)$, $b = 7.7157(2)$, $c = 5.41953(15)$ compared to $a = 5.4596(2)$, $b = 7.6982(4)$, $c = 5.4086(2)$ for NaMgH$_3$ at RT [25]. This change is about two orders of magnitude more than expected from thermal expansion. The Rietveld refinement (Fig. 3a) indicates NaMgH$_{3-x}$F$_x$ with $x = 0.83(4)$. Both phases were present after 5 h of isothermal hydrogen absorption at 325 °C (Fig. S3 in Supporting information). The two main phases were NaBH$_4$, 41.5(2) wt%, and NaMgH$_{3-x}$F$_x$ with $x=0.848(3)$, 24.5(2) wt%, whereas the amounts of MgB$_2$ and NaH$_{1-x}$F$_x$ decreased from 44.5(2) wt% and 51.2(3) wt% with $x = 0.099(1)$ after ball milling to 17.8(1) wt% and 6.9(1) wt% with $x = 0.074(4)$, respectively. This shows that the hydrogenation was not completed. After reaching 325 °C at 50 bar hydrogen, SR-PXD data were collected for 5 h under isothermal conditions (Fig. 1a). A phase similar to the earlier reported boron-rich phase (“B$_{d8}$”) [13] started to form after 6 min at 325 °C. This is an intermediate phase as it disappeared after 135 min at the isothermal condition. The *ex situ* hydrogenation data (Fig. 2c) indicates that 5 h of hydrogenation should lead to the absorption of approximately 5 wt% H. The reaction temperatures are lower than earlier reported in ref [26], where NaMgH$_3$ and NaBH$_4$ were formed at 330 °C and 380 °C, respectively. Our observation that NaBH$_4$ is formed prior to NaMgH$_{3-x}$F$_x$ indicates a changed reaction path because of incorporation of fluorine into the structure.
**Fig. 1** - *In situ* SR-PXD data from the absorption process of NaH + 9 NaF + 5 MgB$_2$ between 25 °C and 325 °C plus a 5 h isotherm (Fig. 1a) and 35 min isotherm (Fig. 1b) at 50 bar H$_2$ are shown. (a) long milled NaF+9NaH+5MgB$_2$; Green Curve (front) showing the formation of NaBH$_4$ at 206 °C and red curve (back) the formation of NaMgH$_{3-x}$F$_x$ at 290 °C. The intermediate boron-rich phase ("B$_{48}$") is also shown. The gap in the data in the isothermal step is due to an accidental interruption of the measurement. $\lambda = 0.80645$ Å. (b) short milled NaF+9NaH+5MgB$_2$; Green Curve (front) showing the formation of NaBH$_4$ and "B$_{48}$" at 268 °C. Red curve (back) the formation of NaMgH$_{3-x}$F$_x$ after 7 min at 325 °C. $\lambda = 0.784624$ Å.
The hydrogenation was repeated ex situ in a Sieverts’ apparatus under the same conditions, but prolonging the isothermal treatments at 325 °C to 41 h. PXD of the hydrogenation product confirms the following reaction:

$$10\text{NaH}_{0.9}F_{0.1(s)} + 5\text{MgB}_{2(s)} + 15.5\text{H}_2(g) \rightarrow 9\text{NaBH}_4(s) + \text{NaMgH}_2F_x(s) + \text{MgH}_2(s) + \text{unknown phase} \quad (1)$$

The Rietveld refinement with the PXD data is shown in Fig. 2a. The observed weight fractions for identified phases of 78.4(2) wt% NaBH₄, 15.1(3) wt% NaMgH₃₋ₓFx with x = 0.35(13) and 6.6(3) wt% MgH₂ are in good agreement with the theoretical fractions from eq. 1 for identified phases as stated above of 78.3 wt%, 15.7 wt% and 6.0 wt%, respectively. In addition there are Bragg peaks from one or more unidentified phases which account for the remaining 3Mg + 1B, corresponding to 16.1 wt% of the sample.

The theoretical hydrogen capacity from eq. 1 is 6.0 wt% which is equal to the observed value from the Sieverts’ measurement. The formation of MgH₂ has been proposed not to be favorable compared to NaMgH₃ [23, 24]. However, the presence of MgH₂ in our ex situ data is in agreement with other experimental data [12, 27].
Rietveld refinement
long milled
*ex situ* absorbed

Rietveld refinement
short milled
*ex situ* absorbed
Fig. 2 - (a) Rietveld refinement to the \textit{ex situ} PXD data after hydrogenation in the Sieverts' apparatus at RT showing experimental (circles) and calculated (red line) patterns, and a difference plot (below) for the long milled NaF+9NaH+5MgB$_2$ after 41 h at 325°C. Vertical ticks mark the Bragg peak positions for (from top): Fe, MgH$_2$ (6.6(3) wt%), NaMgH$_{3-x}$F$_x$ (15.1(3) wt%, $x = 0.35(13)$) and NaBH$_4$ (78.4(2) wt%). $R_{wp} = 5.48\%$ and (b) Rietveld refinement for the short milled NaF+9NaH+5MgB$_2$ after 41 h at 325°C. Vertical ticks mark the Bragg peak positions for (from top): Fe, MgH$_2$ (9.5(2) wt%), NaMgH$_3$ (8.5(1) wt%) and NaBH$_4$ (82.1(2) wt%). $R_{wp} = 2.58\%$; (c) \textit{ex situ} hydrogenation of NaF+9NaH+5MgB$_2$ at 325 °C and 50 bar H$_2$ pressure. The total hydrogen contents achieved for short milled and long milled system are 6.3 wt\% and 6.0 wt\%, respectively.

**Hydrogenation of short milled NaF+9NaH+5MgB$_2$**

During the \textit{in situ} hydrogenation with heating rate 5 C min$^{-1}$ and 50 bar H$_2$ pressure of the short milled sample the boron-rich phase ("B$_{48}$") was already formed at 268 °C during heating, and minor Bragg peaks from NaBH$_4$ appeared simultaneously (Fig. 1b, green curve). Weak Bragg peaks from NaMgH$_3$$_{3-x}$F$_x$ was first observed in the isothermal regime after 9 min at 325 °C (Fig. 1b, red curve). This is in contrast to what was observed in the case of the long milled composite where NaBH$_4$ and NaMgH$_3$$_{3-x}$F$_x$ appeared first and "B$_{48}$" was an intermediate phase. After 35 min isothermal hydrogenation at 325 °C, "B$_{48}$" became a major hydrogenation product together with NaMgH$_3$$_{3-x}$F$_x$. We assume the presence of the "B$_{48}$" phase is the main reason why NaBH$_4$ and NaMgH$_3$$_{3-x}$F$_x$ are formed at higher temperatures compared to the long milled composite.
The ex situ hydrogenation data (Fig. 2c) at 50 bar hydrogen and 325 °C for the short milled sample gives a hydrogen uptake of 3 wt% after 1.5 h hydrogenation (1h heating + 35 min isotherm). This is surprising, as the in situ hydrogenation products in Fig. 3a, NaBH₄ and NaMgH₃₋ₓFₓ, are only minor phases with refined weight fractions of 4.2(1) wt% and 4.9(1) wt%, respectively, after the same hydrogenation time. If these two phases with the observed amounts were the only hydrogenation products, it would correspond to a hydrogen uptake of only 0.3 wt % H for the composite. Hence, it seems likely that the “B₄₈” phase is a hydrogenation product that contains most of the absorbed hydrogen. Another possible explanation is that non-crystalline phases absorb hydrogen and form non-crystalline products, although this seems less likely as no appreciable diffuse scattering is observed in the SR-PXD data.

The boron-rich “B₄₈” phase was observed in both composites. Rietveld refinements with the structure model from ref. [13] yielded unphysically high temperature factors and thus a large overestimation of its phase fraction. This was taken as an indication that the structure model is not complete, as already suggested by Pistidda et al. [13]. Thus the phase was fitted with Le Bail (i.e. structureless) refinements, and is not accounted for the reported phase compositions of the samples. During hydrogenation this phase was reported to form prior to NaMgH₃ [13], in agreement with our observation for the short-milled composite. In contrast “B₄₈” was formed after NaMgH₃₋ₓFₓ during the reaction in the long milled composite, and it disappeared after 3 h hydrogenation at 325 °C.

During the in situ hydrogenation at 50 bar of the short milled sample a pressure reduction was observed during the formation of “B₄₈”, which support the assumption that this phase contained hydrogen in addition to boron. It is supported by the ex situ Sieverts’ data (Fig. 2c), which showed a rapid hydrogen uptake during the first 1.5 h. According to the in situ SR-PXD data “B₄₈” was formed during the first 1.5 h of hydrogenation. Preparation of an isotope substituted sample (¹¹B and D) for powder neutron diffraction is planned to clarify the nature of “B₄₈”.

The repeated ex situ hydrogenation in the Sieverts’ apparatus under the same conditions, with an isothermal treatment at 325 °C for 41 h, leads to the assumption that the reaction pathway in the short milled composite is slightly different. The following reaction eq. 2 is proposed based on the hydrogenation products shown and refined with the data in Fig. 2b:

\[
9\text{NaH} + \text{NaF} + 5\text{MgB}_2 + 16.875\text{H}_2 \rightarrow 9.25\text{NaBH}_4 + 0.75\text{NaMgH}_3 + 1.75\text{MgH}_2 + \text{non-crystalline}
\] (2)
The refined weight fractions for identified phases of 82.1(2) wt% NaBH$_4$, 8.5(1) wt% NaMgH$_3$ and 9.5(2) wt% MgH$_2$ are in agreement with the theoretical weight fractions from eq. 2 for identified phases as stated above of 80.7 wt%, 8.7 wt% and 10.6 wt%, respectively. The incorporation of fluorine into the lattice of NaMgH$_3$ was not observed. The remaining amounts of 2.5Mg, 1F and 0.75B are assumed to be in amorphous and/or nanocrystalline phase since no unidentified phases are observed (non-crystalline = 16.8 wt%). The theoretical hydrogen capacity from eq. 2 is 6.5 wt% if the non-crystalline phase is not hydrogen-containing. This amount coincides with the observed value of 6.3 wt% from the Sieverts’ measurement. The formation of MgH$_2$ has been proposed not to be favorable compared to NaMgH$_3$ [23, 24]. However, the presence of MgH$_2$ in our ex situ data is in agreement with other experimental data [12, 27].

The amount of absorbed hydrogen is more than 65 % higher than reported earlier at the same conditions and time, 3.8 wt%, for a fluorine-free composite [14]. Moreover, the kinetics are greatly improved. In the work by Pistidda et al. it took 2 h to obtain 2 wt% H and 63 h to reach 6.2 wt% at 25 bar. In our experiment at 50 bar, 4 wt% was absorbed after 2 h and 6.3 wt% after 41 h at 325 °C.

Rietveld refinements with SR-PXD data of in situ hydrogenation for the short- and long-milled samples with a heating rate 5 °C min$^{-1}$ from RT to 325 °C and 35 min or 55 min isotherm at 325 °C, respectively, are shown in Fig. 3a and b. The amounts of the hydrogenation products are larger in the long milled composite with 26.6(3) wt% NaBH$_4$ and NaMgH$_{3-x}$F$_x$ 12.2(1) wt%, compared to 4.2(1) and 4.9(1) wt%, respectively, in the short-milled composite. "B$_{48}$" is fitted with Le Bail refinement (see above). The differences between the composites could be explained by the different particle sizes obtained by the different milling times.
Fig. 3 - Rietveld refinement plot from SR-PXD patterns at 325 °C showing experimental (circles) and calculated (red line) patterns, and a difference plot (below) for the (a) short milled NaF+9NaH+5MgB₂ after 35 min at 325°C. Vertical ticks mark the Bragg peak positions for (from top): "B₄₈" (Le Bail fit), NaMg₃₋ₓFₓ (4.9(1) wt%, x = 0.81(19)), Fe (1.2(1) wt%), NaH (43.4(1) wt%), NaBH₄ (4.2(1) wt%) and MgB₂ (46.3(1) wt%); R_wp = 4.68%; \( \lambda = 0.784624 \) Å; and (b) long milled NaF+9NaH+5MgB₂ after 55 min at 325°C Vertical ticks mark the Bragg peak positions for (from top): "B₄₈" (Le Bail fit), NaMg₃₋ₓFₓ (12.2(1) wt%, x = 0.83(4)), Fe (6.9(1) wt%), NaH (18.0(1) wt%), NaBH₄ (26.6(3) wt%) and MgB₂ (36.4(2) wt%); R_wp = 4.2%, \( \lambda = 0.80645 \) Å.
Dehydrogenation of long milled NaF+9NaH+5MgB₂

After 5 h of in situ hydrogenation followed by cooling to RT under 50 bar H₂, the long milled sample was decomposed in situ. From RT to 200 °C the sample was heated with 20 °C min⁻¹, then further to 510 °C with 5 °C min⁻¹ and finished with an isothermal step for 1 h at 510 °C. 1 bar hydrogen backpressure was applied at the start of the dehydrogenation process. The desorption shown in Fig. 4 is characterized by two main steps. Step 1 is from RT to approx. 400 °C and step 2 from 400 °C to 510 °C plus 1 h of isothermal treatment.

Step 1: Both NaH and NaBH₄ started to disappear at 366 °C and disappeared completely at 378 and 402 °C, respectively. Diffuse scattering is increased as the Bragg peaks from these phases are decreased in intensity, probably due to a molten NaH:NaBH₄ eutectic. This is in agreement with earlier results showing a molten mixture of NaH and NaBH₄ that is present at 383 °C for 5 and 50 bar H₂ [28]. This is below the melting points of both NaH at 400 °C [29] and NaBH₄ at 505 °C [30].

Step 2: Mg appeared at 391 °C and disappeared at 507 °C. The amount of NaMgH₃xFₓ is decreasing between 385 and 450 °C. From 450 °C it is present as a minority phase and the amount did not decrease further. The Bragg peaks from Mg decreased from 480 °C while those from MgB₂ increased in intensity. At 507 °C the remaining Bragg peaks from Mg and the diffuse scattering from the NaH:NaBH₄ melt disappeared abruptly with a corresponding increase in the Bragg peak intensities from MgB₂. FeB was observed at 450 °C and the intensity in these Bragg peaks increased until the iron contaminant had been consumed after 15 min at 510 °C. Because of the FeB formation in the long milled sample the data in Fig. 4 cannot be directly compared with the short milled sample.

After 50 min at 510 °C the amounts of MgB₂ and NaMgH₃xFₓ were not changing any further. NaMgH₃ is reported to be stable up to 500 °C at 10 bar H₂ [24]. The presence of NaMgH₃xFₓ as a minority phase at 510 °C at 1 bar H₂ indicates a stabilizing effect by fluorine substitution.
**De- and re-hydrogenation of short milled NaF+9NaH+5MgB₂**

The *in situ* decomposition SR-PXD measurement of the short milled sample followed the *in situ* hydrogenation described above by lowering the pressure to 1 bar and heating from 325 to 510 °C at 5 °C min⁻¹. A 1 h isothermal step was applied at the end of the heating ramp. The SR-PXD data are shown in Fig. 5a. Bragg peaks from NaBH₄ and “B₄8” decreased from 325 °C and disappeared at 353 °C (grey line in Fig. 5a). The Bragg peaks corresponding to NaMgH₃ₓFₓ were decreasing along with those from NaH₁₋ₓFₓ until the peaks from both phases disappeared at 491 °C. This is above the melting point of NaH (400 °C [29]), thus indicating a stabilizing effect of fluorine substitution. After the Bragg peaks from NaH₁₋ₓFₓ disappeared, diffuse scattering appeared, indicating melting of NaH₁₋ₓFₓ. The molten NaH₁₋ₓFₓ and Mg in a nanocrystalline state were probably responsible for the reappearance of weak Bragg peaks from NaMgH₃ₓFₓ. This process stopped when Bragg peaks of Mg appeared at 495 °C. After 60 min at 510 °C the intensities of the Bragg peaks from Mg, MgB₂ and NaMgH₃ₓFₓ did not change any
further. The stabilizing effect of the fluorine substitution in NaMgH$_{3-x}$F$_x$ and NaH$_{1-x}$F$_x$ is again evident.

The *in situ* re-hydrogenation started with cooling from 510 to 325 °C with a rate of -5 °C min$^{-1}$ (1 bar H$_2$ backpressure) and at 325 °C 50 bar of hydrogen was introduced (blue line in Fig. 5b). Fig. 5b shows that NaBH$_4$ crystallized at 368 °C (orange line) before hydrogen pressure was increased (blue line). The yield was 52.5(2) wt% (Fig. S4 in Supporting information). Since NaBH$_4$ was only present in a minor amount after the first hydrogenation (Fig. 3a), it is clear that NaBH$_4$ must have been formed in a hydrogenation process in the melt under 1 bar H$_2$. This is in agreement with earlier observation that a higher amount of NaBH$_4$ is appearing for hydrogenation at rather low pressures of 5 bar hydrogen compared to higher pressures of 25 or 50 bar hydrogen [14]. Our recrystallization temperature for NaBH$_4$, 368 °C, is in excellent agreement with the literature value of 363 °C [14]. Both “B$_{48}$” and NaBH$_4$ appeared at 268 °C during the first *in situ* hydrogenation, and disappeared at the same temperature during *in situ* desorption. Thus it can be suggested that both phases are formed and consumed in the same reactions.

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**Fig.5 -** (a) *In situ* decomposition of short milled NaF+9NaH+5MgB$_2$. Heating ramp from 325 to 510 °C at 5 °C min$^{-1}$ and an isothermal step of 1 hour at 1 bar hydrogen backpressure. (b) *In situ* re-hydrogenation of short milled NaF+9NaH+5MgB$_2$. Cooling ramp from 510 to 325 °C at -5 °C min$^{-1}$ at 1 bar hydrogen backpressure and 50 bar hydrogen applied at 325 °C. A darker color corresponds to a higher diffraction intensity.
Conclusions and Outlook

The hydrogen sorption properties of the 2NaH+MgB$_2$-system was enhanced by adding 10 mol% NaF. The theoretical hydrogen capacity of the investigated systems NaF+9NaH+5MgB$_2$ is 7.7 wt% with the formation of 10NaBH$_{3.9}$F$_{0.1}$ + 5MgH$_2$. A different reaction pathway resulting in the hydrogenation products NaBH$_4$, MgH$_2$ and NaMgH$_{3-x}$F$_x$ (0≤x≤1) gives an *ex situ* measured hydrogen capacity of 6.0 wt% for the long milled composite (Sieverts’ apparatus). *Ex situ* hydrogenation of the short milled composite at the same conditions resulted in a hydrogen uptake of 6.3 wt% H, with a slightly different reaction pathway as the long milled composite.

The thermodynamics of this system have been modified compared to the non-fluorinated systems investigated by Nwakwuo et al. [26] and Pistidda et al [14], especially when taking into consideration that the formation of NaBH$_4$ which is reported to start at 380 °C is decreased to 206 °C and 268 °C in our long milled sample and short milled sample, respectively.

The boron-rich phase “B$_{48}$” appeared in both samples. In the short milled sample it constitutes a major crystalline phase after 1.5 h, whereas it disappeared in the long milled sample after 3 h of hydrogenation. The “B$_{48}$” phase was not found after *in situ* re-hydrogenation in the short milled sample, as NaBH$_4$ is formed instead as the major phase with a fraction of 52.5(2) wt% at low pressures of approx. 1 bar H$_2$.

The composition of the boron-rich “B$_{48}$” is still not clear, but there are strong indications that it contains hydrogen in addition to boron. Neutron diffraction measurements will be conducted to clarify the nature of this phase.

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References


Supporting Information

**Title:** Milling time effect of Reactive Hydride Composites of NaF-NaH-MgB₂ investigated by *in situ* powder diffraction

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Fig. S1: Rietveld refinement plot from SR-PXD patterns at RT after ball milling showing experimental (circles) and calculated (red line) patterns, and a difference plot (below) for the long milled NaF+9NaH+5MgB₂. Vertical ticks mark the Bragg peak positions for (from top): NaH₁ₓFₓ (51.2(3) wt%, x = 0.099(1)), Fe (4.3(1) wt%) and MgB₂ (44.5(2) wt %); Rwp = 4.43 %.
Fig. S2: Rietveld refinement plot from SR-PXD patterns at RT after ball milling showing experimental (circles) and calculated (red line) patterns, and a difference plot (below) for the short milled NaF+9NaH+5MgB$_2$. Vertical ticks mark the Bragg peak positions for (from top): Fe (0.5(1) wt%), NaF (2.9(3) wt%), NaH$_{1-x}$F$_x$ (59.6(6) wt%, $x = 0.078(1)$) and MgB$_2$ (37.1(1) wt%); $R_{wp} = 3.94\%$. 
Fig. S3: Rietveld refinement plot from SR-PXD patterns at RT after 5 h isothermal hydrogenation at 325 °C showing experimental (circles) and calculated (red line) patterns, and a difference plot (below) for the long milled NaF+9NaH+5MgB₂. Vertical ticks mark the Bragg peak positions for (from top): NaH₁ₓFₙ (6.9(1) wt%, x = 0.074(4)), Fe (9.2(1) wt%), MgB₂ (17.8(1) wt%), NaMgH₃₋ₓFₓ (24.5(2) wt%, x = 0.848(3)) and NaBH₄ (41.5(2) wt%); Rwp = 3.73 %.
Fig. S4: Rietveld refinement plot from SR-PXD patterns at RT after 1 h isothermal re-absorption at 325 °C showing experimental (circles) and calculated (red line) patterns, and a difference plot (below) for the short milled NaF+9NaH+5MgB\textsubscript{2}. Vertical ticks mark the Bragg peak positions for (from top): Mg (3.2(1) wt%), NaMg\textsubscript{3-x}F\textsubscript{x} (3.8(8) wt%, x = 1), Fe (0.038(7) wt%), NaH\textsubscript{1-x}F\textsubscript{x} (14.5(1) wt%, x = 0.71), NaBH\textsubscript{4} (52.5(2) wt%) and MgB\textsubscript{2} (26.0(2) wt%); $R_{wp} = 8.72\%$. 

Supporting information – S4