Synthesis and thermal decomposition of Mg(BH₄)₂–TMO (TMO=TiO₂;ZrO₂;Nb₂O₅;MoO₃) composites

I. Saldan¹,², I. Llamas-Jansa¹, S. Hino¹, C. Frommen¹, B.C. Hauback¹*
¹Institute for Energy Technology, Physics Department, Box 40, NO-2027 Kjeller, Norway
²Ivan Franko National University of Lviv, Department of Physical and Colloid Chemistry, 6 Kyryla and Mefodiya Str., UA-79005, Lviv, Ukraine
E-mail: Bjorn.Hauback@ife.no

Abstract
Ball-milling has been applied to prepare composites between γ-Mg(BH₄)₂ and several transition metal oxides (TMO=TiO₂;ZrO₂;Nb₂O₅;MoO₃). No chemical interaction between Mg(BH₄)₂ and the TMO was observed during composite preparation and only a partial amorphization of γ-Mg(BH₄)₂ was detected. Complete decomposition of Mg(BH₄)₂ into crystalline MgB₂ was found above 500 ºC for all composites. The used TMOs with exception of ZrO₂ were chemically converted to oxides with lower oxidation states and the corresponding borides during the thermal decomposition of Mg(BH₄)₂.

1. Introduction
Magnesium borohydride is one of the most promising hydrogen storage materials though its kinetics and reversibility are still main challenges. The decomposition of Mg(BH₄)₂ occurs via several stages [1-4]. Different magnesium polyboranes appear depending on the process conditions. The most stable intermediate is magnesium dodecaborane, MgB₁₂H₁₂, which eventually transforms into MgB₂. The geometrical similarity of the boron icosahedral frame-work in MgB₁₂H₁₂ and that of bulk boron can be a reason for the kinetic stability of the dodecaborane [5] that by-turn may hamper rehydrogenation. Apparently, the synthesis of Mg(BH₄)₂ from lower polyboranes might be possible at reasonable hydrogen pressure and temperature [6]. A catalyst that prevents the dodecaborane formation may be one of the possibilities to improve the reversibility of Mg(BH₄)₂ dehydrogenation. Therefore development of effective additives for the improved decomposition/formation of Mg(BH₄)₂ is one of the most important problems to solve before its practical application. High valence transition metal compounds with carbon, nitrogen, oxygen or halogenide ligands have the ability to form bonds to hydrogen with varying stoichiometries. This encourages the fast dissociation into atomic hydrogen or its recombination to hydrogen molecules [7]. An optimum stability of the transition metal compounds can be found in some oxides which are less stable than corresponding carbides or nitrides but more stable than corresponding halogenides.

In the present paper transition metal oxides (TMO) are studied as a possible catalyst for the Mg(BH₄)₂ decomposition in the prepared Mg(BH₄)₂–TMO (TMO=TiO₂;ZrO₂;Nb₂O₅;MoO₃) composites.

2. Experimental part
Commercial γ-Mg(BH₄)₂ (≥95%, Sigma Aldrich) was used to prepare Mg(BH₄)₂–TMO (TMO=TiO₂;ZrO₂;Nb₂O₅;MoO₃) composites in molar ratios of 1:0.02. Rutile (TiO₂) (99.90%, Sigma Aldrich), ZrO₂ (97.7%, Merck), Nb₂O₅ (99.99%, Sigma Aldrich) and MoO₃ (99.5%, Sigma Aldrich) were chosen as additives. The as-received powders were milled for 1 h using a planetary micro mill (Fritsch pulverisette 7) in argon atmosphere (speed 300 rpm). New stainless steel balls 10 mm in size, with a 40:1 balls-to-powder ratio, were used. The balls were cleaned by standard procedure and dried by technical fan. All handling and preparation of the samples took place in a MBraun UniLab glove box with continuously purified argon atmosphere where oxygen and moisture values were less than 1 ppm.

Powder X-ray diffraction (PXD) was performed in a Bruker AXS D8 Advance instrument fitted with a Göbel mirror and a LynxEye™ 1D detector. The samples were encapsulated in 0.8 glass capillaries sealed with glue in the glovebox. Data acquisition was performed with a step size of 0.02° and 2s/step measurement time in range of 5-65° for 2Θ. The structure data base implemented in the Eva program was used for phase analysis.

Differential scanning calorimetry (DSC) and thermo-gravimetrical analysis (TGA) was performed simultaneously using a Netzsch STA 449 F3 Jupiter instrument. Samples were measured inside aluminum crucibles fitted with pierced lids. Argon with a flow rate of 50 ml/min was used as a purge gas. Experiments were performed between room temperature (RT) and 500 °C using a heating rate of 2 °C/min.

Temperature-programmed desorption (TPD) coupled with residual gas analysis (RGA) was used to estimate gas release. The samples were installed in a sealed copper sample holder. Experiments were carried out under vacuum (~10⁻⁴ mbar) with a heating rate of 2 °C/min from RT to 500 °C.

3. Results and discussions
The prepared Mg(BH₄)₂–TMO (TMO=TiO₂;ZrO₂;Nb₂O₅;MoO₃) composites were analyzed by PXD, DSC and TPD (Figs. 1-4). Based on PXD experiments the ball milled composites were similar to a physical mixture of Mg(BH₄)₂ and corresponding oxides powder (Fig.1). No indication for a chemical interaction between Mg(BH₄)₂ and the additives was found under the current milling conditions. Partial amorphization of magnesium borohydride was observed after 1 h of ball-milling through an increase of the background below 25° in 2Θ (Fig. 1). Similar findings have been reported in [8] where it was concluded that Mg(BH₄)₂ decomposition is hardly affected by ball milling. In addition we observe that the level of amorphization depends on the nature of the additives. PXD analysis confirms that the smallest changes in the background is observed for Mg(BH₄)₂–ZrO₂ composite. This finding might be explained by the high hardness of ZrO₂ (8 in Mohs scale) and thermodynamic stability (ΔH°f = −1080 kJ/mol) [8]. Changes of diffraction peaks (lower intensity and peak broadening) might be the result of a reduced particle size in the prepared composites.
DSC experiments for the Mg(BH$_4$)$_2$–TMO (TMO=TiO$_2$;ZrO$_2$;Nb$_2$O$_5$;MoO$_3$) composites and pure Mg(BH$_4$)$_2$ are presented in Fig. 2. Because of the partial amorphization of Mg(BH$_4$)$_2$ in the composites their DSC curves show a small exothermic peak at above 100 °C due to recrystallization. For pure γ-Mg(BH$_4$)$_2$ two endothermic peaks are observed at ~165 °C and ~195 °C which can be attributed to the γ→ε and ε→β phase transformations [9]. The exothermic peak at ~320 °C corresponds to the crystallization of amorphous MgH$_2$ and the two endothermic signals at ~309 and ~333 °C can be assigned to the decomposition of Mg(BH$_4$)$_2$, and the decomposition of MgH$_2$ into magnesium metal and hydrogen gas, respectively [10]:

\[
\begin{align*}
\text{Mg(BH}_4\text{)}_2 & \rightarrow 3\text{H}_2 + 2\text{B} + \text{MgH}_2\text{(amorph)} \quad \text{(309 °C)} \\
\text{MgH}_2\text{(amorph)} & \rightarrow \text{MgH}_2\text{(cryst)} \quad \text{(320 °C)} \\
\text{MgH}_2\text{(cryst)} & \rightarrow \text{Mg} + \text{H}_2 \quad \text{(333 °C)}
\end{align*}
\]

The Mg(BH$_4$)$_2$–ZrO$_2$ composite shows a thermal behavior similar to that of pure Mg(BH$_4$)$_2$. The other prepared composites show a small shift in the order of ~10-20 °C towards higher temperatures for decomposition of MgH$_2$ (Eq. 3).
TPD analysis of Mg(BH$_4$)$_2$–TMO (TMO=TiO$_2$;ZrO$_2$;Nb$_2$O$_5$;MoO$_3$) composites showed gas release during temperature development (Fig. 3). There are three main events of hydrogen release for pure Mg(BH$_4$)$_2$. The most intense peak is observed at ~300 °C and other at ~333 and ~355 °C. Only for Mg(BH$_4$)$_2$–ZrO$_2$ composite these three events had similar intensity but were shifted to lower temperature by ~10 °C. Since the signal at ~165 °C is attributed to a small hydrogen release during the $\gamma \rightarrow \varepsilon$ phase transformation, it might be concluded that for Mg(BH$_4$)$_2$–ZrO$_2$ composite the Mg(BH$_4$)$_2$ phase undergoes a low amorphization. The TPD curves for Mg(BH$_4$)$_2$–TMO (TMO=TiO$_2$;MoO$_3$) showed a different intensity distribution as compared to pure Mg(BH$_4$)$_2$ and Mg(BH$_4$)$_2$–ZrO$_2$ although the temperatures were similar to those of pure Mg(BH$_4$)$_2$. Gas release of Mg(BH$_4$)$_2$–Nb$_2$O$_5$ composite was combined in one main signal but shifted to higher temperature.
The Mg(BH$_4$)$_2$–TMO (TMO=TiO$_2$;ZrO$_2$;Nb$_2$O$_5$;MoO$_3$) composites and pure Mg(BH$_4$)$_2$ were studied again by PXD after thermal decomposition (Fig. 4). For all the samples PXD experiments confirm the complete decomposition of Mg(BH$_4$)$_2$ into crystalline MgB$_2$ after TPD carried out till ~500 °C. A small amount of CuO as an impurity phase (most probably from the copper sample holder) was detected, and its peak positions have been indicated by tickmarks in Fig. 4. In addition, all of the used TMOs with the exception of ZrO$_2$ were chemically converted into oxides with lower oxidation states and the corresponding borides. This implies that a chemical reaction between Mg(BH$_4$)$_2$ and the TMOs has occurred during heating and only ZrO$_2$ remains unaffected by this reaction.
4. Conclusions
The current experimental work on the synthesis and thermal decomposition of Mg(BH$_4$)$_2$–TMO (TMO=TiO$_2$;ZrO$_2$;Nb$_2$O$_5$;MoO$_3$) composites leads to the following main conclusions:

1. There is no chemical interaction between γ-Mg(BH$_4$)$_2$ and the additives under the applied milling procedure while some amorphization for γ-Mg(BH$_4$)$_2$ is observed by an increase of the background intensity at 2θ<25º. The smallest change in the background is observed for Mg(BH$_4$)$_2$–ZrO$_2$ composite;

2. Positions of DSC peaks of Mg(BH$_4$)$_2$–ZrO$_2$ composite are very similar to that of pure γ-Mg(BH$_4$)$_2$. A small shift by ~10 ºC to higher temperatures is observed for the DSC traces of the others composites;

3. There are three main gas release events (~300; 333 and 355 ºC) for pure γ-Mg(BH$_4$)$_2$ that are shifted to lower temperatures by ~10 ºC for the Mg(BH$_4$)$_2$–ZrO$_2$ composite. The composites containing TiO$_2$, Nb$_2$O$_5$ and MoO$_3$ show changed TPD curves that are furthermore shifted to higher temperatures;

4. All transition metal oxides with the exception of ZrO$_2$ react with γ-Mg(BH$_4$)$_2$ at high temperatures and are chemically converted into oxides with lower oxidation state and the corresponding transition metal borides.

The present results suggest that of all the TMOs tested only ZrO$_2$ might act as a catalyst during Mg(BH$_4$)$_2$ decomposition since it is not chemically altered.

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