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# Composite behaviour of MgH<sub>2</sub> and complex hydride mixtures synthesized by ball milling

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#### ABSTRACT

In the present work, the MgH<sub>2</sub>–LiAlH<sub>4</sub> and NaBH<sub>4</sub>–MgH<sub>2</sub> hydride composites were synthesized by mechanical ball milling. The phase structure and morphology were investigated by XRD and SEM. The hydrogen desorption characteristics of obtained composites were measured by DSC. It is shown that the hydrogen desorption temperature of the composite constituent with the higher desorption temperature in the systems, decreases linearly with increasing volume fraction of the constituent having lower desorption temperature. It is demonstrated that the hydrogen desorption in the hydride composites involves two steps: first, the lower temperature hydride decomposes to metal or complex hydride + metal and H<sub>2</sub> and in a subsequent step, these intermediary compounds, catalyze or thermodynamically change the decomposition of the high temperature hydride. The thermodynamic destabilization can be an effect of solid solution or intermediate intermetallic phase formation. Sometimes both phenomena such catalytic influence and intermetallic phase formation can be observed.

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#### 1. Introduction

The investigation of materials that match the DOE criteria for hydrogen storage systems to be used in automotive industry has been largely focused on hydride composites in the past 20 years. One of the most promising systems considered for automotive application was magnesium based composite destabilized by the formation [1–7] or addition of intermetallic phases [8–14]. In this case the low temperature decomposition counterpart acts as a catalyst which does not decrease dramatically the total capacity of the system. Quite different approach based on thermodynamical destabilization of complex hydrides has been proposed in last decade. In particular, since the work of Vajo et al. [15,16] on LiBH<sub>4</sub>–MgH<sub>2</sub> mixture, there have been a number of publications devoted to complex and metal hydrides that are thermodynamically or catalytically destabilized by ball milling with others hydrides [17–20].

Recently, it has been shown [18,19] that the hydrogen desorption temperature of the composite constituent with the higher desorption temperature in the systems, substantially decreases linearly with increasing volume fraction of the constituent having lower desorption temperature.

In the present work the composite approach is applied to the  $MgH_2 + LiAlH_4$  and  $NaBH_4 + MgH_2$  systems. The composites with various volume fractions of both constituents were processed by controlled ball milling (CBM) in a magneto-mill (under hydrogen or argon atmosphere). Hydrogen desorption was tested using a differential scanning calorimeter (DSC) analysis. The aim of this work is to analyze the influence of metal and complex hydride additives on high temperature counterparts' hydrogen decomposition process in  $MgH_2 + LiAlH_4$  and  $NaBH_4 + MgH_2$  composites.

#### 2. Experimental

As-received commercial MgH<sub>2</sub> powder (purchased from ABCR GmbH&Co.KG; ~98 wt.% purity) as well as NaBH<sub>4</sub> (98% purity) and LiAlH<sub>4</sub> (97% purity) hydride powders both from Alfa Aesar were mixed to MgH<sub>2</sub> + X wt.% LiAlH<sub>4</sub> and NaBH<sub>4</sub> + Y wt.% MgH<sub>2</sub> (where X = 10, 30 and 50; Y = 10, 20, 50, 70, 80 and 90) compositions. As a reference MgH<sub>2</sub> and NaBH<sub>4</sub> without additives were used.

For the reference MgH<sub>2</sub> powder and the MgH<sub>2</sub>–LiAlH<sub>4</sub> composites continuous controlled mechanical milling (CMM) was carried out for 10 h in hydrogen under ~400 kPa pressure in the magneto-mill Uni-Ball-Mill 5 (A.O.C. Scientific Engineering Pty Ltd., Australia), using a high energy shearing with two NdFeB external magnets mode. The balls-to-powder weight ratio was ~40 and the rotational speed of milling vial was ~175 rpm. The NaBH<sub>4</sub> reference powder and NaBH<sub>4</sub>–MgH<sub>2</sub> composites were synthesized by milling for 20 h in argon under similar milling conditions.

Morphological examination of powders was conducted with high-resolution, field emission SEM (FE SEM) LEO 1530 and SEM Philips microscope LaB<sub>6</sub> XL-30.

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Fig. 1. The morphology of reference (a) MgH<sub>2</sub> and (b) NaBH<sub>4</sub> powders as well as (c) MgH<sub>2</sub> + 50 wt.% LiAlH<sub>4</sub> and (d) NaBH<sub>4</sub> + 50 wt.% MgH<sub>2</sub> composites after ball milling.

The phase structure of as milled and reference powders was characterized by Seifert and Rigaku Rotaflex D/Max B rotating anode powder diffractometers. Monochromated  $CoK\alpha_1$  and  $CuK\alpha_1$  radiations, respectively, were used in this study.

The thermal behaviour of powders was studied by differential scanning calorimetry (DSC) (SETARAM Labsys<sup>TM</sup>) and PERKIN ELMER DSC7 with heating rate of 5, 10, 15 and 20 °C/min and argon flow rate of 20 ml/min. Activation energy of hydrogen desorption  $E_a$  was estimated using Kissinger's plot. The samples were tested in a DSC almost immediately after completion of milling to avoid aging phenomena due to hydrolysis of composite components.

#### 3. Results and discussion

#### 3.1. Morphology of $MgH_2$ + LiAlH<sub>4</sub> and NaBH<sub>4</sub> + MgH<sub>2</sub> composites

The morphology of reference  $MgH_2$  and  $NaBH_4$  matrix powders after ball milling are presented in Fig. 1a and b. Fig. 1c and d shows typical SEM micrographs of milled ( $MgH_2 + LiAlH_4$  and  $NaBH_4 + MgH_2$ ) composite powders with weight percentage of additive materials of 50 wt.%.

After milling for 10 h the average particle size of MgH<sub>2</sub> is reduced from ~30  $\mu$ m (as-received powder) to ~1.7  $\pm$  1.2  $\mu$ m for reference materials (Fig. 1a) and composites containing 10 and 30 wt.% LiAlH<sub>4</sub> (not presented in this work). For composites modified by 50 wt.% of LiAlH<sub>4</sub> (Fig. 1.c) the average particle size is reduced to ~3.5  $\pm$  2.7  $\mu$ m. It suggests that lithium alanate might act as a lubricant during MgH<sub>2</sub> ball milling and particle size reduction is much less effective when the level of LiAlH<sub>4</sub> additive reaches 50 wt.%.

The particles of as-received sodium borohydride powder which characterizes by irregular shape and average size around 145  $\mu$ m, after milling, showed visible refinement for both reference (Fig. 1b) and composite materials with MgH<sub>2</sub> of 50 wt.% (Fig. 1d). The particle size of MgH<sub>2</sub> seems to be slightly reduced and the particles are uniformly distributed in a volume of NaBH<sub>4</sub> particles.

The composites having higher contents of MgH<sub>2</sub> (more than 50 wt.%; not presented in this work) show visible particle size reduction (~40 times). It is clearly seen that milling conditions are strongly dependent on composite composition. The efficiency of milling process (MgH<sub>2</sub> particle size reduction) is much higher for composites with higher magnesium hydride content.

# 3.2. The phase structure of $MgH_2 + LiAlH_4$ and $NaBH_4 + MgH_2$ composites

Fig. 2a shows the XRD patterns of the 10, 30 and 50 wt.% LiAlH<sub>4</sub> composites after milling. The crystal structure of investigated composites consists of primarily MgH<sub>2</sub> and LiAlH<sub>4</sub> with Li<sub>3</sub>AlH<sub>6</sub>. Similar effect was reported by Andreasen et al. [21]. After 6 h of milling they observed the appearance of additional peak on XRD pattern due to the formation of either monoclinic or rhombohedral Li<sub>3</sub>AlH<sub>6</sub> which suggests the partial decomposition of pure LiAlH<sub>4</sub> during milling.

Fig. 2b shows the XRD patterns for the NaBH<sub>4</sub> + MgH<sub>2</sub> composites with a varying content of magnesium hydride. The intensity of particular peaks is related to chemical composition, but it must be pointed out that the  $\gamma$ -MgH<sub>2</sub> phase, typical for magnesium hydride after milling, appears only when the level of MgH<sub>2</sub> is 50 wt.% This verifies SEM observations, that milling process for MgH<sub>2</sub> phase starts to be effective only for composites having high content of magnesium hydride.

#### 3.3. Thermal behaviour of MgH<sub>2</sub> + LiAlH<sub>4</sub> composites

The thermal behaviour of studied composites was tested by DSC method. Fig. 3a shows a quantitative evaluation of the destabilization efficiency of MgH<sub>2</sub> hydride caused by LiAlH<sub>4</sub> additive. The peak temperature of the hydrogen desorption from MgH<sub>2</sub> as measured in DSC for composites is plotted as a function of the LiAlH<sub>4</sub> content. There is no doubt that the MgH<sub>2</sub> desorption temperature only slightly decreases linearly from ~355 to 325 °C with increasing LiAlH<sub>4</sub> content from 10 to 50 wt.%, respectively. The coefficient of fit amounts to 0.99. Also, it was found that even small amount of LiAlH<sub>4</sub> additive (10 wt.%) reduces in visible way the MgH<sub>2</sub> decomposition temperature form  $\sim$  395 °C for reference material (MgH<sub>2</sub> milled without additive) to ~355 °C for magnesium hydride destabilized by 10 wt.% of lithium alanate. Moreover it was found that volume of lattice cell for Mg observed after decomposition test decreases rapidly in the sample modified by 20 wt.% LiAlH<sub>4</sub> and then its value is irrelevant to alanate content (Fig. 3a). It suggests



**Fig. 2.** XRD patterns of (a)  $MgH_2$ -LiAlH<sub>4</sub> and (b)  $NaBH_4 + MgH_2$  composites after ball milling. (I)  $MgH_2 + 50$  wt.% LiAlH<sub>4</sub>; (II)  $MgH_2 + 30$  wt.% LiAlH<sub>4</sub>; (III)  $MgH_2 + 10$  wt.% LiAlH<sub>4</sub>; (IV)  $NaBH_4 + 90$  wt.%  $MgH_2$ ; (V)  $NaBH_4 + 80$  wt.%  $MgH_2$ ; (VI)  $NaBH_4 + 70$  wt.%  $MgH_2$ ; (VII)  $NaBH_4 + 50$  wt.%  $MgH_2$ ; (VIII)  $NaBH_4 + 20$  wt.%  $MgH_2$ ; (IX)  $NaBH_4 + 10$  wt.%  $MgH_2$ .

aluminum solid solution formation in magnesium lattice in the range up to 20 wt.%.

The DSC curves obtained for test with various heating rate were used for estimation of the activation energy of MgH<sub>2</sub> decomposition using well-known Kissinger method for phase transformations. The influence of LiAlH<sub>4</sub> complex hydride on energy of activation is presented in Fig. 3b. It is clearly visible that there is no functional relation between the activation energy of hydrogen desorption from the MgH<sub>2</sub> constituent in a composite and its composition. Regardless, to the LiAlH<sub>4</sub> concentration in analyzed system the energy of activation decreases from ~180 kJ/mol for milled reference MgH<sub>2</sub> to ~140 kJ/mol for composite powders.

Therefore, it is apparent that the decrease of DSC peak temperature is not related to activation energy which does not decrease with the same rate with increasing content of the LiAlH<sub>4</sub> complex hydride. In addition, this behaviour strongly suggests that the effect of LiAlH<sub>4</sub> additive on thermodynamics and can be related to solid solution formation (Fig. 3a)

#### 3.4. Thermal behaviour of $NaBH_4 + MgH_2$ composites

Fig. 4a presents the temperatures for the melting and decomposition peaks of NaBH<sub>4</sub> as a function of MgH<sub>2</sub> content in a composite. The melting temperature of NaBH<sub>4</sub> only slightly decreases linearly with increasing content of MgH<sub>2</sub>. The decomposition temperature of NaBH<sub>4</sub> behaves in a more complex fashion. The MgH<sub>2</sub> additive in the range of 0–20 wt.% does not change the decomposition temperature of NaBH<sub>4</sub>. Increasing the amount of magnesium hydride over 20 wt.% gradually reduces the decomposition temperature of NaBH<sub>4</sub> which is eventually reduced by ~200 °C for the



Fig. 3. DSC decomposition peak temperature of the  $MgH_2$  constituent in the  $MgH_2$ -LiAlH<sub>4</sub> composites (a) and energy of activation (b) as a function of LiAlH<sub>4</sub> content.

 $NaBH_4 + 90$  wt.%MgH<sub>2</sub> composite. According to Vajo et al. [15,16] this kind of behaviour in a mixture of two hydrides could be caused by the formation of an intermetallic phase, which could change the enthalpy of the system. By analogy to the reaction presented by Vajo et al. [15,16] for LiBH<sub>4</sub> destabilized by MgH<sub>2</sub> the decomposition of the (NaBH<sub>4</sub> + MgH<sub>2</sub>) composite could proceed as follows:

$$2NaBH_4 + MgH_2 \rightarrow 2NaH + MgB_2 + 4H_2$$
(1)

It suggests that the strongest destabilization of NaBH<sub>4</sub> by MgH<sub>2</sub> should be observed for a composite where the yield of MgB<sub>2</sub> formation is the highest and that means for the stoichiometric composition (NaBH<sub>4</sub>+25.8 wt.% MgH<sub>2</sub>). In Fig. 4a the yield of MgB<sub>2</sub> formation versus composite chemical composition and theoretically predicted products of decomposition are presented. For hypo-stoichiometric compositions the composites in this range should decompose to solid products such as NaH, MgB<sub>2</sub> and B. Stoichiometric decomposition is characterized by the presence of only NaH and MgB<sub>2</sub>. The hyper-stoichiometric composites decompose to NaH, MgB<sub>2</sub> and Mg. These theoretical phase compositions of decomposed composites are confirmed for the hyper-stoichiometric NaBH<sub>4</sub> + 50 wt.% MgH<sub>2</sub> composite. To obtain a sufficient amount of powder for X-ray diffraction, the decomposition process of the above-mentioned composite was conducted in a furnace rather than in a DSC apparatus, under Ar atmosphere and at temperature of 600 °C. The XRD pattern of the analyzed products of decomposition is presented in Fig. 4b. It shows the presence of the peaks of the MgB<sub>2</sub> and MgO phases. It seems that the conditions of the decomposition process carried out in a furnace were insufficient to prevent the oxidation of decomposition product Mg. No Bragg peaks of NaH are observed in Fig. 4b. The decomposition temperature of NaH is quoted by Grochala and Edwards [22] as



**Fig. 4.** Melting and decomposition DSC peak temperatures of the NaBH<sub>4</sub> constituent in the NaBH<sub>4</sub> + MgH<sub>2</sub> composites as a function of MgH<sub>2</sub> content as well as (b) XRD pattern for NaBH<sub>4</sub> + 50 wt.% MgH<sub>2</sub> composite after decomposition at 600 °C.

425 °C. If NaH indeed decomposed to metallic Na and hydrogen at the furnace temperature of 600 °C then as a very low melting point metal (~100 °C) it might have evaporated at such a high temperature and its Bragg peaks would not be observed in Fig. 4b. In Fig. 4a the decomposition temperature of NaBH4 decreases linearly with increasing MgH<sub>2</sub> content only for hyper-stoichiometric composites. In contrast to the theory presented of Vajo et al. [15,16] and the decomposition temperature of NaBH<sub>4</sub> in the hypo-stoichiometric composites does not exhibit any increase with increasing content of MgH<sub>2</sub> as it would have to if their theory was correct (increase of MgB<sub>2</sub> content). However, it must be noticed that destabilization process described by the above authors is based on the perceived enthalpy changes. Even if NaBH<sub>4</sub> would be destabilized thermodynamically, it might have not easily decomposed due to poor kinetics. Therefore, an alternative hypothesis is that the free Mg formed due to the decomposition of MgH<sub>2</sub> could act as a catalyst to increase the kinetics of decomposition of NaBH<sub>4</sub> whether or not it is destabilized thermodynamically.

#### 4. Conclusions

The DSC hydrogen desorption peak temperature of the  $MgH_2$  constituent in the  $MgH_2$  + LiAlH<sub>4</sub> composite decreases linearly with increasing weight fraction of complex hydride component. For the system magnesium hydride/lithium alanate there is no functional dependence between energy of activation of  $MgH_2$  decomposition and content of LiAlH<sub>4</sub>. It was found that lithium alanate thermodynamically affects process of  $MgH_2$  decomposition by formation of solid solution (aluminum dissolved in magnesium matrix).

The catalytic effects of  $MgH_2$  additives on the hydrogen desorption properties of the  $NaBH_4$  formed after controlled milling of the ( $NaBH_4 + MgH_2$ ) composites have been studied. The DSC desorption peak temperature of  $NaBH_4$  decreases dramatically with increasing amount of  $MgH_2$  in the composites. This effect is most likely due to the catalytic effect of Mg which is formed during  $MgH_2$ decomposition.

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