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Role of Additives in LiBH4-MgH2 Reactive Hydride Composite sorption reactions

Role of Additives in LiBH$_4$-MgH$_2$ Reactive Hydride Composites for Sorption Kinetics

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Abstract

The influence of additives on the reaction kinetics and for microstructure refinement in LiBH$_4$-MgH$_2$ composites is investigated in detail. Indications on the rate limiting processes during the reactions are obtained by comparison of the measured reaction kinetics to simulations with one specific rate limiting process. The kinetics of the sorption reactions are derived from volumetric measurements as well as from *in-situ* X-ray diffraction (XRD) measurements. During desorption, the hydrogen is released at a constant rate, which possibly is correlated to the one-dimensional growth of MgB$_2$ platelets. In contrast, the kinetic curves of the absorption reactions exhibit the typical shape of contracting-volume controlled kinetics. The microscopical interpretation of kinetic measurements are supported by transmission electron microscopy (TEM) images confirming the formation of additive-nanostructures in the grain boundaries upon cycling. The present investigations underline the importance of the additives as nucleation substrates and the influence of the microstructure on the reaction kinetics.

Introduction

Hydrogen is a promising energy carrier for future applications, because of its high energy content as well as its compatibility to a comprehensive clean-energy concept.

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One of the limitations for application is the lack of a safe and efficient storage option at present. Besides liquid and compressed gas storage, metal hydrides can store hydrogen safely and reversibly at high volumetric densities. However, at present, no single metal hydride fulfils the requirements posed for mobile applications regarding both, gravimetric density and suitable reaction enthalpies. Reactive Hydride Composites (RHC) offer a promising solution for the thermodynamic- and capacitive challenges[1-4]. The overall reaction enthalpy in these systems is lowered by the exothermic formation of a new compound during the endothermic desorption reaction of two or more hydrides. This concept is well established by now and has been extended to several systems [1-9]. For the present work, the system of $2LiBH_4 + MgH_2 \leftrightarrow 2LiH + MgB_2 + 4H_2$ is investigated in detail. The reactions show strong kinetic constraints and therefore take place at elevated temperatures only. However, with suitable transition-metal based additives a reduction of the reaction time by a factor of 10 was achieved in comparison to the pure composite material [10].

Previous work on the chemical state of transition-metal based additives indicated the formation of transition-metal borides during synthesis or cycling [11-13]. Anomalous small angle X-ray scattering [11] and EXAFS analysis [13] further hinted towards the formation of rather small nanoparticles of the respective transition-metal compounds. Their presence has now been confirmed for Zr-based additives by TEM and the results are shown in this publication. Characterization of the additives in the initial and cycled composites was a first step towards understanding the function and mechanism of the additives. In this work, the reaction kinetics of ab- and desorption reactions are analyzed qualitatively with regard to the rate limiting processes and the effect induced by the additives is discussed. Analyzing the measured reaction kinetics with microstructural models, the specific rate limiting step of the growth process can be deduced, which can be, for example, limited by interface velocity or diffusion in case of volumetric growth or

contracting volume (in various dimensions). Thereby, a comprehensive model for the function and mechanism of transition metal based additives and the sorption reactions in general is derived.

Experimental

The initial $LiBH_4$, MgH_2, LiH and MgB_2 powders and the additives were purchased from Alfa Aesar with the highest available purity. For the investigations of the initially hydrided composites $LiBH_4$-MgH_2, the as-received MgH_2 was premilled for 5 hours in a Spex 8000M Mixer Mill. Afterwards, $LiBH_4$ and the additives were added and milled for additional 5h with a ball to powder ratio of 10:1. For comparison, the initially dehydrided composite LiH-MgB_2 and the additives were directly milled for 5h. Various transition metal chlorides and isopropoxides or oxides such as $ZrCl_4$, Zr-isopropoxide, isopropanol complex, VCl_3, V-triisopropoxide-oxide, $TiCl_3$, $TiCl_4$ Ti-isopropanol, Sc_2O_3 and surplus MgB_2 as well as surplus LiH were investigated as additives. For all milling experiments, a 50ml hardened steel vial was used and a sample mass of 5g and a ball to powder ratio of 10:1 was selected. All handling and milling was performed under a continuously purified argon atmosphere.

The volumetric measurements were perfomed using a Sievert's type apparatus designed by HERA Hydrogen Systems, Quebec, Canada. Standard conditions for the present measurements were 400°C and 5 bar hydrogen for desorption and 350°C and 50 bar hydrogen for absorption.

In-situ XRD measurements were performed in transmission mode at I711 of the MAX-lab, Lund, Sweden [14]. The samples were mounted in single crystal sapphire tubes under inert conditions in an Argon filled glove box. The diffracted intensity was measured using a MAR 165 CCD plate detector. The X-ray wavelength was λ=1.06474Å.

The sample is heated by a tungsten wire below the capillary and the temperature is controlled by an inserted thermocouple and controlled by an external PID regulator. Details of the experimental setup are given in [15]. For the present experiments, the sample was kept under 150 bar hydrogen and 265°C for several hours. Quantitative analysis of ongoing reactions was achieved by systematically integrating the intensity and correcting for baseline of single diffraction maxima for each phase and scan.

For the TEM analysis, the cross-sectional TEM samples were obtained from the specific interest region of each sample by a dual-beam focussed ion beam (FIB) (FEI, Nova 200) equipped with a manipulating probe (100.7[TM], Omniprobe). A TEM sample preparation process using FIB and airlock loading chamber without air-exposure is described in details in [16]. Using this technique, TEM samples which have a final thickness of ≈50nm and large observation areas ($10x5\mu m^2$) were obtained. The prepared TEM sample was loaded into a 200keV TEM (FEI, Tecnai F20) using a portable glove-bag under Ar atmosphere (99.999%). Scanning transmission electron microscope (STEM) bright field images were collected using a high-angle annular darkfield (HAADF) detector. The chemical composition of the sample was obtained using energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy EELS. Crystallographic information was obtained by selected area electron diffraction (SAED) patterns.

For analysis of the rate limiting processes during the sorption reactions a qualitative approach was followed by comparing the measured reaction kinetics to calculated values of known rate limiting processes. The applied models can be divided in three main groups [17-20]. An overview over the applied equations and a short description is given in table 1. In a first model, the transformed fraction $\alpha(t)$ is directly proportional to time. This is the case for a constant reaction rate, which is typically found for one dimensional growth and it is, e.g., found in hydrides when splitting and recombination of hydrogen at the surface limits the sorption reactions [17-20].

The second group of models describes the growth of existing nuclei by the Johnson-Mehl-Avrami (JMA) approach. Nucleation occurs randomly in the bulk of the material. The growth can be controlled by an interface reaction, leading to a constant interface velocity or by a diffusion controlled growth mechanism with a decelerating interface velocity. The kinetics is relatively independent of size and distribution of the reacting particles.

The third group of models describes the growth of a new phase from the surface to the centre of a spherical volume; they are called contracting-volume models. Here, an existing thin layer of reacted material on the surface grows inwards. The reaction itself can be again interface or diffusion controlled.

The transformed fraction $\alpha(t)$ in correlation to time is calculated by normalization from the measurements. This calculated transformed fraction is then substituted in the equations. The equations are formed in such a way, that if the assumed process limits the reaction, a linear behaviour with time should be observed. The quality of the match is judged by the passing of a linear fit through zero and the agreement to the linear fit, the correlation coefficient R should be close to 1.

The equations noted in table 1 were originally derived to describe the reaction kinetics of solid state reactions of single particles but have been successfully adapted to powder particles and metal hydrides [17-22]. The volume change between the desorbed and the hydrided state cannot be neglected, since the hydrides take up approximately twice the volume of the desorbed state. Thus, a rather complex model for contracting volume with decelerating interface velocity geometry is used for the three dimensional growth in contracting volume geometry.

It is emphasized that the reactive hydride composites are not simple binary solid-gas systems but complex reactions with four phases in equilibrium, and significant mass

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transport other than hydrogen takes place. Therefore, the validity of these models cannot be assumed a priori and the obtained results have to be taken cautiously. However, a well matching model can give useful hints to processes, which might limit the reaction. In agreement with the principle of the RHC, the sorption reactions consist of a decomposition reaction and the formation of a new compound, which take place simultaneously. Because of the two step character of the desorption reaction, only the slower second step associated with the decomposition of $LiBH_4$ [10,23] is considered. Furthermore, the first sorption reactions of the composites are neglected, and only cycled samples are evaluated.

Results and discussion:

Absorption reaction:

Figure 1 illustrates the distribution of LiH and MgB_2 in the composites after milling for 5 h in a SPEX mill. The TEM sample was prepared by cutting one slice of a composite particle by FIB. The components LiH and MgB_2 were identified by SAED. EELS-mapping of individual elements shows the distribution of the different phases. Fairly large MgB_2 particles in the size range of 100 up to several hundred nm are embedded in a LiH matrix, forming a composite with finely and homogeneously distributed LiH and MgB_2 within the powder particle.

In figure 2 the reaction kinetics measured in volumetric measurements at 350 °C and 50 bar hydrogen are presented. The curve with the open symbols presents the pure composite, prepared as $LiBH_4$-MgH_2 composite and previous desorption. The curve presented by triangles represents the sample prepared in the same way as the pure composite but with the addition of 10 mol% of MgB_2 as an additive. Since this

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compound is one of the reaction products of the desorption, it is not assumed to influence the reactions chemically but rather to have a microstructural effect. The reaction time is reduced to one half approximately, compared to the pure composite. As a third composite, addition of 5 mol% Sc_2O_3 as a typical transition metal based additive is shown. The reaction time is about one fifth of the reaction time of the pure composite.

In figure 3 the functions $F(\alpha)$ of the experimentally determined transformed fraction α are plotted exemplarily for the first absorption reaction of the pure $LiBH_4$-MgH_2 composite using the models and equations described in table 1. The highest linearity with time (R= 0.99965) and best fit through zero (A= -0.000412) can be observed for the 3-dimensional contracting volume model with interface control. Similar relations were obtained for all absorption reactions, see table 3. In some cases transport processes and diffusion appear to be the rate limiting process. However, this could be subject to changes in the ongoing sorption process because of the increasing diffusion distances and volume relations. These observations are in good agreement with the results from Wan et al. [24] for the first absorption reaction in pure LiH-MgB_2 composites.

As described above, the rate limiting process possibly refers either to the decomposition of MgB_2 and LiH or the formation of MgH_2 and $LiBH_4$. For clarification, isothermal *in-situ* XRD measurements were performed at I711, MAX-lab, Lund, Sweden with initial LiH-MgB_2 composites and analyzed quantitatively with respect to the phase fractions. In the present experiment the pressure was 150 bar hydrogen. The volume of the sample holder and connecting tubes are large in comparison to the sample and heated volume, the hydrogen pressure can therefore be considered constant throughout the experiment. The sample was first heated up to 265 °C and the temperature was then held constant for

5 hours. An overview over the occurring crystalline phases during this experiment is given in figure 4.

The reflections of the initial materials LiH and MgB_2 are identified, e.g., at q values around 2.25, 3.0, 3.5 Å^{-1} for MgB_2 and 2.6 and 3.1 Å^{-1} for LiH with $q = 4\pi \sin\theta / \lambda$, where θ is half the scattering angle and λ the wavelength. The start of the formation of MgH_2 is observed at 265°C. The simultaneous formation of $LiBH_4$ cannot be observed because of its either liquid or amorphous state [24]. The melting point of this compound is 270 °C and a small temperature inaccuracy of around 15 K cannot be excluded. The formation of the crystalline polymorph is confirmed during cooling to room temperature. The evolution of the phase fractions during the sorption reaction is determined quantitatively for MgB_2 and MgH_2 by plotting the normalized peak area over time (figure 5). The smooth correlation of the two phases supports the idea of a single step absorption reaction mechanism, i.e. all partial reactions take place simultaneously from the beginning to the end of the absorption. Analysis of the kinetics using the models described above reveals a contracting volume controlled reaction for both phases. This indicates that the MgB_2 phase is consumed from the surface to the centre.

During absorption, MgB_2 and LiH need to decompose and form MgH_2 and $LiBH_4$. Transport processes including B or Mg and Li have to take place besides hydrogen diffusion. Hydrogen and ion diffusion in LiH and $LiBH_4$ are known to be fast and should not limit the reaction progress [24-26]. Regarding previous work on nanocrystalline MgH_2 [3, 19], it is also not likely, that the formation of MgH_2 is the rate limiting process of the reaction kinetics under the present conditions. Therefore it is proposed that the interface reaction during decomposition of MgB_2 is the rate limiting

step during absorption. As a consequence, the length scales and thus the microstructure of MgB_2 play a key role for the transformation process.

Desorption reaction:

Volumetric measurements of the desorption reaction measured at 5 bar hydrogen and 400°C are presented in figure 6. Desorption occurs in two steps under these conditions. The first can be ascribed to release of hydrogen from MgH_2 forming metallic Mg [10]. After this first and very fast reaction step, the first desorption of the pure $LiBH_4$-MgH_2 composite (open circles with line) shows a rather long incubation period. In this period, no significant amount of hydrogen is released, which excludes, e.g., any diffusion or hydrogen recombination controlled reaction and hints towards hindered nucleation of MgB_2. The second step associated to hydrogen release has been correlated to the simultaneous decomposition of $LiBH_4$ and formation of MgB_2 [10,23]. To experimentally verify that the incubation time corresponds to a retarded nucleation of MgB_2, 10mol% surplus MgB_2 was added to the composite (half-filled triangles in figure 6). Thereby, the incubation period of the first desorption reaction is significantly reduced and the reaction kinetics enhanced if measured under the same conditions as the previous experiments. Further experiments with only 3mol% excess MgB_2 (open triangles) or without pre-milling MgB_2 together with the MgH_2 (stars), led to incubation periods similar to those without additive, see figure 6. Under the assumption that the microstructure of the $LiBH_4$ is not significantly altered by the additives, this proves the importance of the amount and distribution of added MgB_2 seeds for the effect, which is typical for a nucleation limited phase transformation. With additional MgB_2, the reaction rates for desorption after the incubation period are already similar to those with a good transition metal based additive, see the measurements performed with Sc_2O_3 as an additive (half-filled circles). This indicates a similar mechanism. It should be pointed

out, that also the first absorption reaction is enhanced by excess MgB_2 in comparison with the pure system, as described above for figure 2. Transition-metal based additives such as $ZrCl_4$ (asterix) have a substantial influence on the sorption kinetics and no incubation period can be observed for the first desorption reaction.

In comparison to the pure composite, two distinct results can be extracted: (i) the incubation period is significantly reduced or even absent; (ii) the observed reaction rates for the second step of the reaction are much higher than for the pure composite. Previous measurements [11] showed the formation of stable transition-metal borides from the transition-metal based additives and indicated their presence as finely distributed nanoparticles. For the first time they were now directly observed in TEM images for the example of $ZrCl_4$ as an additive in cycled $LiBH_4$-MgH_2 composites, see figure 7. The ZrB_2 nanoparticles are located in the interfaces and grain boundaries, while the MgB_2 grains are embedded in a LiH matrix in the desorbed state. The function of the ZrB_2 nanoparticles to supply nucleation sites suggests itself.

A necessary condition for potent heterogeneous nucleation substrates is the low energy of a coherent interface, which is dominated by the strain caused by the lattice misfits at the interface. Chemical contributions are neclected for the present study. For the present material couples, there is no data available for the interface energies. However, with the criteria from edge-to-edge model [28] the lattice misfits in the rows of close-packed atoms and planes of the two phases can be estimated and evaluated from the crystal structures. The edge-to-edge matching [28-30] is applied to evaluate the heterogeneous nucleation barrier of MgB_2 on various additives (table 2). This model is based on the matching of close or relatively close packed atom rows across the interface between the substrate (additive) and the nucleus (MgB_2). Additionally, these atom rows have to be

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contained in close or relatively close packed planes. The strain energy between substrate and nucleus is significantly minimized, if the misfit of the interatomic spacing is below 10 %. The interplanar mismatch should be below 6 %. Besides the transition-metal borides formed by the additives, LiH and Mg as well as possible compounds from oxygen contamination such as Li_2O and MgO are evaluated. Table 2 shows that ZrB_2, ScB_2, VB_2, TiB_2, MgO and Mg (ranked by increasing misfit) fulfill the edge-to-edge matching condition; i.e. according to this metallic Mg is expected to support MgB_2 nucleation without an incubation period. The heterogeneous nucleation potency of LiH and Li_2O is hindered by a larger interplanar mismatch. It is assumed, that the atom matching occurs on certain low index crystallographic planes of the substrates which fulfil the edge-to-edge matching criterion. Therefore, the morphology of the substrates influences the nucleation potency strongly.

Typically the nucleation occurs at ledge positions. Therefore, not only the two dimensional misfit on the interfacial plane is important, but also the third dimension of the growing phase needs to match the ledge. For example: a favourable pair of interfacial matching planes for MgB_2 nucleation on Mg would be of type (0001)-MgB_2 // (0001)-Mg. Ledges with a prismatic face of type $(10\bar{1}0)$ on these basal Mg planes are not preferential MgB_2 nucleation sites, since the directional misfit in the $<0001>$ direction (third dimension) between both phase is large (approx. 48 %). In the case of MgB_2 nucleation on basal planes of the transition metal borides the misfit in the $<0001>$ direction is significantly smaller ranging from 0.1 % (ZrB_2) to -13.2 % (VB_2). These considerations may explain the favourable effect of transition metal borides on reaction kinetics, i.e. the nucleation of MgB_2 as compared to other phases or additives. It should be noted, that the effect of the improved kinetics with additives is sustainable upon further cycling.

For further elucidation of the reaction mechanisms, the volumetrically obtained reaction kinetics for the second step of the desorption reaction are analyzed with regard to the rate limiting process. Because the behaviour of cycled materials is of more interest, the focus of this study was laid on the second rather than the first desorption. An important boundary condition for all applied models is either a constant nucleation rate or initial presence of all nuclei. This assumption is not valid, if the hampered nucleation of MgB_2 is one of the reaction controlling processes as discussed above. For cycled samples no incubation period was noted, which can be explained by residual MgB_2 present in all reaction states. For most samples, a linear relation of the transformed fraction to time was observed for the second step of the desorption reaction. The results of the kinetic model fitting from all investigated samples (by volumetric measurements) are noted in table 3.

A constant hydrogen release rate is found in most of the desorption measurements (transformed fraction α is proportional to time). This indicates a one-dimensional growth process, e.g. an interface controlled reaction with a constant interface area. The surface area of the particles in the composite is not supposed to be constant because the volume in the desorbed state is about half the volume of the hydrogenated state. A possible constant interface area could be present locally as a constant reaction interface in combination with linear growth of the new phase. Indeed, plate like structures are observed experimentally for MgB_2 in the desorbed composites by TEM measurements, see figure 8. Typical dimensions are observed to be 10 to 20 nm by 50-100nm in the in-plane direction.

Based on these findings, a new mechanism for the phase reaction in reactive hydride composites is proposed and the respective models are sketched in figure 9. The model

takes the observed plate-like growth of MgB_2 into account and explains the observed constant reaction rate during desorption. The plate-like structure of MgB_2 is caused by restricted growth along the c-axis of the MgB_2 crystallites [31]. The models in figure 9 consider the role of the additive during the growth of MgB_2 plates as nucleation agents. In pure composites, unreacted MgB_2 is assumed to take over the role as nucleation substrate after the first cycle.

The crystal structure of the transition metal borides and MgB_2 is similar. Therefore, these borides supply coherent interfaces independent of the crystallographic plane and ledges available for nucleation, and heterogeneous MgB_2 nucleation is favoured. Also growth of the MgB_2 crystals is not restricted to occur parallel to the basal plane of the Mg surface, but can also be performed in other directions. These directions allow much faster and sustainable atomic transport to the interface reaction. It should be noted that because of the small scale additives and the mismatch with respect to the Mg, formation of incoherent interfaces might occur also in this case, favouring atomic transport within the interface. Clearly, the increased number of nucleation sites increases the total area of the reaction interface and thus decreases the overall reaction time significantly. Thereby, the microstructure is refined as well, which positively influences the following absorption reaction.

Conclusions:

Nucleation of MgB_2 is proposed to be a key process for the start of the hydrogen desorption reaction and the respective role of additives is shown. Transition metal borides, which typically form from the chosen transition metal based additives, have the same hexagonal lattice structure as MgB_2. The lattice misfits between the closest packed

planes of MgB_2 and transition metal borides were calculated to be small. The formation of nanostructures of the additives as well as their location in the interfaces upon cycling as proposed in earlier work [11] was verified by TEM measurements for the first time. Although the reaction times are much different with and without additives, analysis of the reaction kinetics indicate that similar reaction processes limit the sorption reactions for all composites, independent of the additive and the initial preparation state. For all absorption reactions, a good agreement with a contracting volume model was observed, which can be explained microscopically by the decomposition of MgB_2. In contrast, most of the analyzed desorption reactions correlate well with a constant reaction rate, indicating an interface controlled one dimensional growth process. Because of the significant mass transport in the composites during the reaction, transport processes and therefore the length scales of the phase separation play a significant role for the reaction kinetics. Transition-metal borides act as heterogeneous nucleation sites for MgB_2, thus avoiding incubation times during desorption and refining the microstructure with favourable consequences for desorption and absorption reaction kinetics.

The study clearly demonstrates that the reactivity of boron compounds (here MgB_2) is a key issue for the sorption kinetics in RHC based on borohydrides. Therefore, those additives play a fundamental role, which refine the microstructure and enhance growth and dissolution of the boride compounds.

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Figure and table captions:

Figure 1: TEM micrograph and EELS mapping of elements of the corresponding region in as milled LiH-MgB$_2$ composites.

Figure 2: First absorption reaction of previously desorbed LiBH$_4$-MgH$_2$ composites measured at 350 °C and 50 bar hydrogen.

Figure 1: Calculated F(α) using the equations in table 1 of the first absorption reaction of LiBH$_4$-MgH$_2$ composites measured volumetrically (see figure 1) at 350 °C and 50 bar hydrogen pressure.

Figure 4: In-situ XRD measurement of the as milled LiH-MgB$_2$ composite, heated from RT to 265 °C and kept isothermal for 5 h under a hydrogen pressure of 150 bar .

Figure 5: Quantitative analysis of the MgB$_2$ and MgH$_2$ fraction measured during the experiment shown in figure 3.

Figure 6: Volumetric measurements of the first desorption reaction of 2LiBH$_4$-MgH$_2$ composites pure (open circles), with 10 mol% additional MgB$_2$ (triangles), 10 mol% additional ZrCl$_4$ and 5 mol% additional Sc$_2$O$_3$. All measurements were performed by heating to 400 °C and holding isothermal then under 5 bar hydrogen pressure.

Figure 7: TEM image of LiH-MgB$_2$ composites with additional 10mol% ZrCl$_4$ after one full sorption cycle.

Figure 8: Boron mapping in cycled LiH-MgB$_2$ composites with 10mol% additional ZrCl$_4$.

Figure 9: Model for plate-like growth of MgB$_2$ during desorption with the assumption that the additive is located in the interface to the Magnesium substrate.

Table 1: Equations, description and label of the applied kinetic models [15].

Table 2: Calculated directional and interplanar misfit between the respective compound and MgB$_2$.

Table 3: Model that best describes the reaction kinetics best in reactive hydride composites with and without additives. X is placed if none of the models gives a satisfactory fit. Multiple models are noted, if they give a very similar and good match. The models placed in brackets give a satisfactory fit.