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Microstructural Study of MgB$_2$ in the LiBH$_4$-MgH$_2$ Composite by Using TEM

Ou Jin $^{1,2}$, Yuanyuan Shang $^3$, Xiaohui Huang $^2$, Xiaoke Mu $^2$, Dorothee Vinga Szabó $^{1,2,4}$, Thi Thu Le $^3$, Stefan Wagner $^1$, Christian Kübel $^{2,4,5}$, Claudio Pistidda $^3$ and Astrid Pundt $^{1,*}$

1 Institute of Applied Materials, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany; ou.jin@kit.edu (O.J.); dorothee.szabo@kit.edu (D.V.S.); stefan.wagner3@kit.edu (S.W.)
2 Institute of Nanotechnology, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany; xiaohui.huang@partner.kit.edu (X.H.); xiaoke.mu@kit.edu (X.M.); christian.kuebel@kit.edu (C.K.)
3 Institute of Hydrogen Technology, Helmholtz-Zentrum Hereon GmbH, 21502 Geesthacht, Germany; yuanyuan.shang@hzg.de (Y.S.); thi.le@hzg.de (T.T.L.); claudio.pistidda@hzg.de (C.P.)
4 Karlsruhe Nano Micro Facility, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany
5 Joint Research Laboratory Nanomaterials, Technical University of Darmstadt, 64206 Darmstadt, Germany
* Correspondence: astrid.pundt@kit.edu; Tel.: +49-721-608-42345

Abstract: The hampered kinetics of reactive hydride composites (RHCs) in hydrogen storage and release, which limits their use for extensive applications in hydrogen storage and energy conversion, can be improved using additives. However, the mechanism of the kinetic restriction and the additive effect on promoting the kinetics have remained unclear. These uncertainties are addressed by utilizing versatile transmission electron microscopy (TEM) on the LiBH$_4$-MgH$_2$ composite under the influence of the 3TiCl$_3$-AlCl$_3$ additives. The formation of the MgB$_2$ phase, as the rate-limiting step, is emphatically studied. According to the observations, the heterogeneous nucleation of MgB$_2$ relies on different nucleation centers (Mg or TiB$_2$ and AlB$_2$). The varied nucleation and growth of MgB$_2$ are related to the in-plane strain energy density at the interface, resulting from the atomic misfit between MgB$_2$ and its nucleation centers. This leads to distinct MgB$_2$ morphologies (bars and platelets) and different performances in the dehydrogenation kinetics of LiBH$_4$-MgH$_2$. It was found that the formation of numerous MgB$_2$ platelets is regarded as the origin of the kinetic improvement. Therefore, to promote dehydrogenation kinetics in comparable RHC systems for hydrogen storage, it is suggested to select additives delivering a small atomic misfit.

Keywords: hydrogen storage; transmission electron microscopy; crystallography; reactive hydride composite; additive

1. Introduction

Hydrogen is a clean and reproducible energy carrier with the highest gravimetric energy density of ~120 kJ g$^{-1}$. For extensive applications of hydrogen, advanced hydrogen storage materials are demanded to store hydrogen safely and efficiently. Reactive hydride composites (RHCs) have been studied intensively due to their exceptionally reversible hydrogen storage capacity [1]. These materials were initially derived from light metal complex hydrides (e.g., LiBH$_4$, LiNH$_2$, NaAlH$_4$, etc.) in combination with a second hydride (e.g., LiH, MgH$_2$, etc.) [2–4]. Among various RHCs, the LiBH$_4$-MgH$_2$ composite is one of the most competitive candidates for both on- and off-board applications, based on the International Energy Agency Task 22 [5]. According to prior studies, the related decomposition reaction occurs in two steps [6]:

$$\text{2LiBH}_4 + \text{MgH}_2 \rightarrow 2\text{LiBH}_4 + \text{Mg} + \text{H}_2 \rightarrow 2\text{LiH} + \text{MgB}_2 + 4\text{H}_2$$  \hspace{1cm} (1)

Compared with the hydrogen capacity of ~18.5 wt% in pristine LiBH$_4$, about 11.4 wt% of hydrogen can still be yielded with the LiBH$_4$-MgH$_2$ composite, while the thermodynamic...
properties are significantly improved by the addition of MgH$_2$, resulting in overall superior performance in hydrogen storage. For LiBH$_4$ alone, the standard enthalpy of decomposition is about 70 kJ mol$^{-1}$ H$_2$ [7]. This value corresponds to a decomposition temperature of about 400 °C under atmospheric pressure [7–9]. For the LiBH$_4$-MgH$_2$ composite, the standard decomposition enthalpy is reduced to about 45 kJ mol$^{-1}$ H$_2$ [9,10], which is ascribed to the exothermic formation of MgB$_2$ during the endothermic two-step decomposition process of the LiBH$_4$-MgH$_2$ composite (see Equation (1)) [3,10]. This results in a notable reduction in the decomposition temperature down to about 170 °C under atmospheric pressure [4,9].

However, in contrast to the thermodynamic predictions, the decomposition of the LiBH$_4$-MgH$_2$ composite for hydrogen release is kinetically limited and barely triggered at moderate temperatures [4,6]. Bösenberg et al. ascribed the sluggish kinetic behavior to the nucleation of MgB$_2$ as the rate-limiting step during dehydrogenation [11,12]. This is prominently reflected in the long incubation period, after the complete decomposition of MgH$_2$ into Mg (the first dehydrogenation step in Equation (1)) and before the massive decomposition of LiBH$_4$ (the second dehydrogenation step in Equation (1)).

Current research on enhancing the kinetics of hydride compounds mainly focuses on nanoconfinement using various carbon scaffolds and on utilizing transition metal-based additives [13–16]. The additives, in particular, provide an impressive boost to the dehydrogenation kinetics of RHCs, with their hydrogen storage capacities being well-preserved. As for the LiBH$_4$-MgH$_2$ composite, it has been reported that the enhanced kinetics can be attributed to a significant promotion of the heterogeneous nucleation of MgB$_2$ by additives [17,18]. However, their role in the decomposition path has not yet been explicitly understood due to a lack of microscopic investigations; thus, the mechanism of MgB$_2$ nucleation and growth in terms of crystallography has remained vague [11]. Complementing the missing knowledge is essential for understanding the reaction process behind the kinetic improvement of the material.

In this study, the additive effect on MgB$_2$ nucleation and growth in the LiBH$_4$-MgH$_2$ composite is clarified by determining the MgB$_2$ morphology and its crystallographic orientations toward nucleation centers. Transmission electron microscopy (TEM) studies were carried out on the microstructural evolution of MgB$_2$ in samples with and without Ti- and Al-based additives using a very high content. This allowed us to reveal the details of how the microstructural boundary conditions determine the decomposition kinetics of the system.

2. Experimental Section

2.1. Material Preparations

The reactants were provided in powder form by the following commercial suppliers: MgH$_2$ (95% purity) from Rockwood Lithium GmbH, LiBH$_4$ (95% purity) from Sigma-Aldrich, and 3TiCl$_3$·AlCl$_3$ (about 76–78% purity) from Fischer Scientific. The LiBH$_4$-MgH$_2$ composite was prepared with a molar content of x% 3TiCl$_3$·AlCl$_3$ (x = 0, 0.625, and 20). The large additive content of 20 mol% is chosen to maximize the additive effect on the MgB$_2$ morphology. To achieve a fine mixing of the reactants and an even dispersion of the additives, the prepared material mixtures (3 g)—namely, 2LiBH$_4$-MgH$_2$ or 2LiBH$_4$-MgH$_2$-3TiCl$_3$·AlCl$_3$—were charged into stainless-steel vials with stainless steel balls in a ball to powder ratio of 20:1. The milling proceeded for 400 min using a Spex 8000 M Mixer Mill. Both the powder handling and milling were always performed under an argon atmosphere in a glovebox (O$_2$, H$_2$O < 0.5 ppm).

2.2. Kinetic Measurements

The volumetric measurements were performed using a custom-built Sievert’s-type apparatus. The milled sample (~170 mg) was charged into the stainless-steel sample holder of the measuring apparatus. The samples were annealed from room temperature to 400 °C at a heating rate of 10 °C min$^{-1}$ under a hydrogen atmosphere of 4 bar. After reaching
the target temperature of 400 °C, the materials were kept under isothermal conditions for several hours.

2.3. XRD Experiments

The ex situ XRD experiments were based on a Bruker D8 Discover diffractometer equipped with a Cu X-ray source (λ = 1.54184 Å) and a 2D VANTEC detector. The operating voltage and current were 50 kV and 1000 mA. The diffraction patterns were acquired in the 2θ range from 10° to 90° with a step size of 0.005°, Δ2θ = 10°, and the exposure time for each step of 400 s. To prevent oxidation phenomena during the acquirement of the XRD pattern, the specimens were sealed in an argon-filled sample holder made of poly (methyl methacrylate) (PMMA).

2.4. TEM Experiments

TEM experiments were performed using a Themis-Z 60-300 (Thermo Fisher Scientific Inc., Waltham, MA, USA) equipped with a monochromator and double aberration correctors (probe and image Cs correctors), operated at 300 kV. TEM sample preparation was carried out under an argon atmosphere in a glovebox (O₂, H₂O < 0.5 ppm). Sample powders were dispersed in toluene and ultra-sonicated for 1 min before being distributed on lacey-carbon coated gold TEM grids S166-A3-V (Ted Pella Inc., Redding, CA, USA). Subsequently, they were transferred under argon from the glovebox into the microscope with a vacuum transfer holder 648 (Gatan Inc., Pleasanton, CA, USA).

The beam current varied from 50 to 100 pA throughout all TEM experiments. Selected area electron diffraction (SAED) patterns, TEM, and high-resolution TEM (HRTEM) images were collected using a OneView camera (Gatan Inc., Pleasanton, CA, USA). Scanning TEM (STEM) images were recorded via a high-angle annular dark-field (HAADF) detector with a convergence angle of 21.5 mrad and a camera length of 93 mm. Energy-dispersive X-ray spectroscopy (EDX) spectrum-imaging (SI) was executed with a Super-X windowless EDX detector (Thermo Fisher Scientific Inc., Waltham, MA, USA) using the same parameters as in STEM mode.

Electron tomography was carried out using a Fischione 2020 tomography holder in STEM mode with the same STEM parameters as mentioned above. HAADF-STEM Tilt series with image dimensions of 2048 × 2048 pixels were collected using Xplore3D (Thermo Fisher Scientific) over a tilt range in increments of 2° from −72° to 78° for the desorbed 2LiBH₄-MgH₂ without additives and from −72° to 68° for the desorbed 2LiBH₄-MgH₂ with 20 mol% 3TiCl₃·AlCl₃. The alignment of the tilt series was performed by IMOD using 10 nm gold colloidal particles as fiducial markers, which leads to the respective mean residual error of 0.736 and 0.129 voxels [19]. The aligned tilt series were then reconstructed using the algorithm simultaneous iterative reconstruction technique (SIRT) with 100 iterations by Inspect3D (Thermo Fisher Scientific) [20]. The 3D visualizations were realized by Avizo 2020.2 (Thermo Fisher Scientific).

In addition, 4D-STEM measurements were carried out in μ probe mode using the OneView camera, with a convergence angle of 0.47 mrad, a camera length of 580 mm, and an acquisition time of 60 ms for each diffraction pattern, and a dose of ~1.5 × 10⁵ e nm⁻². STEM electron energy-loss spectroscopy (EELS) SI was acquired using a Gatan Continuum 970 HighRes imaging filter (GIF) (Gatan Inc., Pleasanton, CA, USA) in dual-EELS mode with 5 ms acquisition time for each low-loss spectrum, 20 ms for each high-loss spectrum, 21.5 mrad convergence angle, 40 mrad collection angle, and 0.3 eV per channel energy dispersion, leading to a measured energy spread of 2.0 eV on the camera. Both the EDX SI and EELS SI data were denoised via principal component analysis (PCA), which effectively reduces the random noise generated during the signal recording [21,22].
3. Results and Discussion

3.1. Material Characterization via XRD and Kinetic Performance

Figure 1a shows the X-ray diffraction (XRD) results of the system 2LiBH₄-MgH₂ with x mol% 3TiCl₃·AlCl₃ (x = 0, 0.625, and 20) in two different states: as-milled and after desorption. In general, no significant variation is visible for the sample without additives and the one containing 0.625 mol% 3TiCl₃·AlCl₃. However, after increasing the additive content to a high value of 20 mol%, the LiBH₄ peaks for the as-milled state and the MgB₂ peaks for the after-desorption state noticeably weakened, whereas strong LiCl peaks appeared for both states. This difference can be attributed to the reaction between LiBH₄ and 3TiCl₃·AlCl₃, which consumed a significant amount of LiBH₄ that is responsible for the generation of MgB₂ [18].

![XRD and kinetic performance graphs](image)

Figure 1. (a) XRD patterns of 2LiBH₄-MgH₂ with x mol% 3TiCl₃·AlCl₃ (x = 0, 0.625, and 20) after milling and after desorption; (b) desorption kinetics of 2LiBH₄-MgH₂ with x mol% 3TiCl₃·AlCl₃ (x = 0, 0.625, and 20) at 400 °C and under 4 bar H₂.

The kinetic performance of the corresponding materials is visualized in Figure 1b. In comparison with the pristine material, the incubation period was reduced from ~25 h to ~8 h with an additive content of 0.625 mol%. By adding 20 mol% 3TiCl₃·AlCl₃, the incubation stage disappeared, and the kinetics of the second desorption step for hydrogen release changed. The reduced hydrogen storage capacity of ~5 wt% for the 20 mol% 3TiCl₃·AlCl₃ sample is due to the significant consumption of LiBH₄ during the reaction with additives.

3.2. MgB₂ Formation without the Influence of Additives

Figure 2a presents the morphology of the decomposed LiBH₄-MgH₂ composite—namely, LiH and MgB₂. The local electron diffraction pattern indicates the existence of MgB₂ crystals with a hexagonal closed packed (hcp) structure (P6m/m, No. 191). The absence of crystallographic information on LiH is likely due to its instability under electron illumination and the low scattering power of Li and H. One impressive feature in Figure 2a is the bar-like morphology of crystals with a parallel arrangement. They were identified as MgB₂ by HRTEM (Figure 2b), its fast Fourier transform (FFT) pattern, and the EDXS elemental map of Mg acquired from the corresponding area in Figure 2a (see Figure S1). The primary growth direction of MgB₂ bars is thus determined to be [1210]MgB₂, which is along the long axis of a MgB₂ bar (the inset in Figure 2b).
Figure 2. The results of 2LiBH$_4$-MgH$_2$ without additives after desorption: (a) STEM-HAADF image and the corresponding electron diffraction pattern; (b) HRTEM image with an inset of the local zoomed-out overview showing the growth direction of MgB$_2$ bars, and the corresponding FFT; (c) volume rendering from tomographic reconstruction of MgB$_2$ bars with an inset showing the corresponding STEM-HAADF image; (d) volume rendering of one selected MgB$_2$ bar chosen from (c).

For a more comprehensive understanding of the MgB$_2$ morphology, electron tomography was conducted. Figure 2c shows a volume rendering of MgB$_2$ bars, reconstructed from the STEM-HAADF tomographic data, and Figure 2d exhibits a single MgB$_2$ bar extracted from the selected region in Figure 2c. It should be noted that MgB$_2$ bars possess a rectangular shape. This can be understood in combination with the study by Lee et al., claiming that a growth constraint exists for MgB$_2$ along the c-axis [0002]$_{\text{MgB}_2}$ [23], which is consistent with our investigation, as the constrained direction [0002]$_{\text{MgB}_2}$ (z-axis in Figure 2d) lays perpendicular to the observed growth direction [1210]$_{\text{MgB}_2}$ (x-axis). Given the rectangular MgB$_2$ bars, another growing direction along the y-axis corresponds to [1010]$_{\text{MgB}_2}$, along which the growth is also limited to some extent. This is discussed in Section 3.5.

The observation of parallel MgB$_2$ bars in Figure 2a implies that their nucleation and growth initially proceeded from the same class of atomic layers of one crystalline nucleation center. Given the two-step decomposition of the LiBH$_4$-MgH$_2$ composite (Equation (1)), Mg and LiBH$_4$ are candidates for this nucleation center. Since LiBH$_4$ has a melting point of approximately 275 °C and, therefore, remains in the liquid state during the desorption at 400 °C, Mg has to be the nucleation center for the heterogeneous nucleation of these MgB$_2$ bars. Another requirement for the nucleation center is that it has to provide a sufficiently large superficial plane to nucleate several MgB$_2$ bars with a lateral size of about 200 nm (Figure 2d). The observed Mg grains are large enough, with a size up to about 1 µm to meet this requirement (see Figure S2).

3.3. MgB$_2$ Formation under the Influence of Additives

To reveal the additive’s effect on MgB$_2$ nucleation and growth, an overdose of 20 mol% 3TiCl$_3$·AlCl$_3$ was taken for the LiBH$_4$·MgH$_2$ composite. Figure 3a shows the material morphology after desorption. According to the XRD result (Figure 1a) and the local electron diffraction pattern (Figure 3a), the element Mg exists only as MgB$_2$. Therefore, the Mg EDX map (Figure 3b) can be directly regarded as representing the distribution of MgB$_2$, along with its growth constraint.
which is comparable with the bright contrast in the HAADF image (Figure 3b). In general, the MgB$_2$ morphology changed significantly, compared with what was previously reported in Section 3.2.

Figure 3. The results of 2LiBH$_4$-MgH$_2$ with 20 mol% 3TiCl$_3$·AlCl$_3$ after desorption: (a) STEM-HAADF image and the corresponding electron diffraction pattern; (b) STEM-HAADF image of the selected area in (a) and EDXS elemental map of Mg (yellow), Ti (blue), and Al (red); (c) volume rendering from tomographic reconstruction of a MgB$_2$ hollow tube viewed at different angles; (d) surface rendering of the cross-section of (c); (e) surface rendering of a segmented MgB$_2$ platelet selected from (d).

Figure 3c exhibits a reconstructed volume rendering of MgB$_2$ in different directions. In this case, two different MgB$_2$ morphologies can be distinguished. Orienting along the x-axis, the parallel-lying MgB$_2$ bars grow into a hollow tube. Inside the tube, the second morphology of platelet-like MgB$_2$ can be identified. It can be seen in Figure 3d that these MgB$_2$ platelets grow from the tube walls of MgB$_2$ bars in a more or less random orientation. For a closer look at these MgB$_2$ platelets, one piece was cut out from Figure 3d and displayed as a segmented surface rendering in Figure 3e. In contrast to the rectangular shape of the MgB$_2$ bars, these MgB$_2$ platelets with a lateral size of about 500 nm possess a more irregular or semi-circular shape. In other words, no primary growth direction is
observed for the MgB$_2$ platelets. In addition, the MgB$_2$ morphology of the sample with 0.625 mol% 3TiCl$_3$·AlCl$_3$ can be found in Figure S3 for comparison.

The platelet-like MgB$_2$ morphology hints at another nucleation center that facilitates the formation of the MgB$_2$ platelets. We suggest that this nucleation center stems from the additives, so the identification and location of these additives is another point of interest. As reported by T.-T. Le et al., the additive 3TiCl$_3$·AlCl$_3$ can react with LiBH$_4$ and generate either AlTi$_3$ or TiB$_2$ and AlB$_2$ [18]. Accordingly, rather than the initial additive 3TiCl$_3$·AlCl$_3$, these reaction products are considered to be the heterogeneous nucleation centers for the MgB$_2$ platelets. Based on the STEM-EDX map in Figure 3b, both Ti and Al are dispersed inside the MgB$_2$ tube, which is also indicative of their role as the nucleation center (also see Figure S4).

For further studies, the EELS SI was acquired. Figure 4a displays the summed elemental map based on the EEL spectrum in Figure 4b, comprising B K-edge in red, Ti L$_{2,3}$-edge in blue, and Mg K-edge in yellow (Figure 4c). Therefore, the orange platelets that result from an overlap between Mg (yellow) and B (red) indicate the elemental correlation between Mg and B and suggest the location of MgB$_2$. Furthermore, the background-subtracted B K-edge recorded in the orange area exhibits a pre-peak at about 190 eV (Figure 4b). This fine structure is evidence of a high and unfilled p-like density of states of Boron, which indicates the bonding between Mg and B and verifies the existence of MgB$_2$ [24].

Similarly, the purple agglomerates in Figure 4a represent the spatial elemental correlation between Ti (blue) and B (red), which disperse around the orange MgB$_2$ platelets. According to the HRTEM image and its FFT pattern (Figure 4d), the presence of TiB$_2$ rather than AlTi$_3$ can be confirmed already after the ball milling process. The HRTEM image corresponding to the purple agglomerates in Figure 4a can be found in Figure S5, which shows a further growth of TiB$_2$ particles up to ~20 nm after desorption likely due to Ostwald ripening. The beneficial effect of TiB$_2$ on accelerating the decomposition of the LiBH$_4$-MgH$_2$ composite was already reported by some studies, which also supports our characterizations [25,26]. Since AlB$_2$ and TiB$_2$ have the same space group (P6m/m, No. 191), with almost the same lattice constants, AlB$_2$ might have the same effect as TiB$_2$, although they cannot be distinguished here.

In Figure 5, the relationship between the crystallography and the morphology of the MgB$_2$ bars and MgB$_2$ platelets is revealed via 4D-STEM. Figure 5b–e provide local electron-diffraction patterns acquired from areas B–E in Figure 5a. A fragment of the MgB$_2$ bar with a rectangular shape can be found in area B of Figure 5a, with the short axis along [10$ar{1}$0]$_{\text{MgB}_2}$ (Figure 5b). Figure 5d,e indicate the long axis direction of the MgB$_2$ bars being along [1$ar{2}$10]$_{\text{MgB}_2}$. These investigated orientations are consistent with Figure 2. Thus, it can be summarized that the morphology of MgB$_2$ bars with a rectangular shape has the long axis direction oriented along [1$ar{2}$10]$_{\text{MgB}_2}$, the short axis direction along [10$ar{1}$0]$_{\text{MgB}_2}$, and the thin direction along [0002]$_{\text{MgB}_2}$. For MgB$_2$ platelets, the thin direction of a platelet, which is also regarded as the growth-restricted direction, is along [0002]$_{\text{MgB}_2}$ (Figure 5a,c). This growth restriction observed for more other MgB$_2$ platelets can be seen in Figure S6.
Figure 4. The results of 2LiBH₄-MgH₂ with 20 mol% 3TiCl₃∙AlCl₃: (a) summed EELS elemental map, based on the background-subtracted EEL spectrum (b), and comprising the elemental distribution of B K-edge (red), Ti L₂,₃-edge (blue), and Mg K-edge (yellow) (c). The inset of a TEM bright-field image was recorded in the same area. In (a), the orange color is coming from the overlap between yellow and red, and is thus indicative of the correlation between Mg and B. Similarly, the color purple stands for the correlation between Ti and B. (d) HRTEM image of TiB₂ (and AlB₂) nanoparticles just after milling and the corresponding FFT of the inset showing the lattice of a single-crystalline TiB₂ particle.
5a,c). This growth restriction observed for more other MgB\textsubscript{2} platelets can be seen in Figure 5. The results of 2LiBH\textsubscript{4}-MgH\textsubscript{2} with 20 mol\% 3TiCl\textsubscript{3}·AlCl\textsubscript{3} after desorption: (a) STEM-HAADF image with insets of magnified areas B and C; (b–e) diffraction patterns acquired in the corresponding areas B–E in (a), which show the crystallographic orientation of MgB\textsubscript{2} bars and platelets.

3.4. Analysis of Orientation Relationships

Given the small size of TiB\textsubscript{2} or/and AlB\textsubscript{2} nanoparticles only up to about 20 nm (Figure S5) and the complexity of the overlapping phases, the interface between the nucleation centers and MgB\textsubscript{2} cannot be investigated in the experiment. For this reason, their orientation relationships (ORs) cannot be experimentally determined in a conventional way by focusing on the interface. To determine the orientation relationship between the different nucleation centers and MgB\textsubscript{2}, we took advantage of the edge-to-edge matching model [27–31].

The edge-to-edge matching model builds on minimizing the energy of coherent interfaces between two adjacent materials, in this case, the nucleation center and the nucleating particle [27,30]. According to this model, the heterogeneous nucleation between the two phases is controlled by their interatomic misfit and their interplanar mismatch. The interatomic misfit is determined along the matching directions of the two phases. These matching directions are selected among their close or nearly close-packed directions identified by the linear atomic density. The interplanar mismatch (d-value mismatch) is determined between the matching planes, which are chosen from the close or nearly close-packed planes. As a rule of thumb, the interatomic misfit and the interplanar mismatch should generally not exceed 10% and 6%, which are regarded as the critical values [27]. On the other hand, minimizing the interatomic misfit has a higher priority than the d-value mismatch from an energetic perspective. A slight excess of the d-value mismatch above 6% is still acceptable, which can be subsequently refined by an additional rotation between the two phases about their matching directions [30].

Since MgB\textsubscript{2}, Mg, and TiB\textsubscript{2} (and AlB\textsubscript{2}) have a similar hexagonal close-packed (hcp) crystal structure, their close or nearly close-packed directions and planes are similarly indexed. Based on their crystallographic characteristics, there are four possible close-packed directions \{10\overline{1}0\}, \{0002\}, \{1\overline{2}10\}, and \{1\overline{1}23\} and four possible close-packed planes \{10\overline{1}0\}, \{10\overline{1}1\}, \{0002\}, and \{1\overline{2}10\} [29]. According to our observations, two distinct MgB\textsubscript{2} morphologies were introduced:

1. Rectangular-shaped MgB\textsubscript{2} bars that are constrained along \[0002\]\textsubscript{MgB\textsubscript{2}} and \[10\overline{1}0\]\textsubscript{MgB\textsubscript{2}}, and primarily grow along \[1\overline{2}10\]\textsubscript{MgB\textsubscript{2}} from Mg grains (Figures 2 and 5);
2. Semi-circular shaped MgB$_2$ platelets that are constrained along [0002]$_{\text{MgB}_2}$ and grow from TiB$_2$ (and AlB$_2$) nanoparticles (Figures 3–5).

Given the large interatomic misfit of (0002)$_{\text{MgB}_2}$, compared with the close-packed directions of Mg and TiB$_2$ (and AlB$_2$) (see Tables S1 and S2), (0002)$_{\text{MgB}_2}$, as one of the close-packed planes, is supposed to be the matching plane for the heterogeneous nucleation of both MgB$_2$ bars and MgB$_2$ platelets on Mg and TiB$_2$ (and AlB$_2$).

For the MgB$_2$ bars, the interplanar mismatch of (0002)$_{\text{MgB}_2}$ concerning the possible matching plane of Mg is listed in Table 1. The only suitable matching planes with a reasonably low interplanar mismatch of ~8.5% are (0002)$_{\text{MgB}_2}$ || (1210)$_{\text{Mg}}$. In addition, since the matching (0002)$_{\text{MgB}_2}$ the plane should include the matching direction, only (10$\overline{1}$0)$_{\text{MgB}_2}$ and (1210)$_{\text{MgB}_2}$ fit for the matching direction. Similarly, only (10$\overline{1}$0)$_{\text{Mg}}$ and (0002)$_{\text{Mg}}$ are fitting for Mg, with (1210)$_{\text{Mg}}$ being the matching plane. The resulting pairs of the matching directions with an interatomic misfit smaller than 10% turn out to be (10$\overline{1}$0)$_{\text{MgB}_2}$ || (10$\overline{1}$0)$_{\text{Mg}}$ and (10$\overline{1}$0)$_{\text{MgB}_2}$ || (0002)$_{\text{Mg}}$ (Table 2). For a refined matching, a tilting angle between (0002)$_{\text{MgB}_2}$ and (1210)$_{\text{Mg}}$ should also be considered (see Figure S7a,b).

In summary, the possible orientation relationships between MgB$_2$ and Mg are predicted to be as follows:

\[
\langle 10\overline{1}0 \rangle_{\text{MgB}_2} \parallel \langle 10\overline{1}0 \rangle_{\text{Mg}} \quad \langle 0002 \rangle_{\text{MgB}_2} \sim 2.0^\circ \text{ from } \langle 1210 \rangle_{\text{Mg}} \\
\langle 10\overline{1}0 \rangle_{\text{MgB}_2} \parallel \langle 0002 \rangle_{\text{Mg}} \quad \langle 0002 \rangle_{\text{MgB}_2} \langle /m\alpha > \text{ from } \langle 1210 \rangle_{\text{Mg}}
\]

Table 1. The interplanar misfit between MgB$_2$ [0002] and possible match planes of Mg nucleation center (%).

| MgB$_2$/Mg | [0002] || [1011] | [0002] || [0002] | [0002] || [0002] |
|------------|----------------|----------------|----------------|----------------|----------------|
|            | 39.8           | 48.6           | 58.4           | 8.5            |

Table 2. The interatomic misfit along possible matching directions between MgB$_2$ and Mg nucleation center (%).

| MgB$_2$/Mg | [10\overline{1}0] || [10\overline{1}0] | [10\overline{1}0] || [0002] | [1210] || [10\overline{1}0] | [1210] || [0002] |
|------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|            | –4.2           | 2.1            | –80.8          | –69.5          |

The orientation relationships between MgB$_2$ and TiB$_2$ (and/or AlB$_2$) can be derived in the same way. The related interplanar mismatch is given in Table 3. In this case, it appears that (0002)$_{\text{MgB}_2}$ pairing with (0002)$_{\text{TiB}_2}$ (and/or (0002)$_{\text{AlB}_2}$) results in the least mismatch.

Table 3. The interplanar misfit between MgB$_2$ [0002] and possible match planes of MB$_2$ (M = Ti or Al) nucleation center (%).

| MgB$_2$/MB$_2$ | [0002] || [1011] | [0002] || [0002] | [0002] || [0002] |
|----------------|----------------|----------------|----------------|----------------|----------------|
| TiB$_2$        | –15.8          | 8.2            | –49.2          | 13.9           |
| AlB$_2$        | –15.5          | 7.6            | –47.9          | 14.6           |

According to Table 4, the possible matching direction are (10$\overline{1}$0) and (1210) for both MgB$_2$ and TiB$_2$ (and/or AlB$_2$). The least interatomic misfit is thus obtained for the matching directions (10$\overline{1}$0)$_{\text{MgB}_2}$ || (10$\overline{1}$0)$_{\text{TiB}_2}$ (AlB$_2$) and (1210)$_{\text{MgB}_2}$ || (1210)$_{\text{TiB}_2}$ (AlB$_2$). Considering

\[
\langle 10\overline{1}0 \rangle_{\text{MgB}_2} \parallel \langle 10\overline{1}0 \rangle_{\text{TiB}_2} (\text{AlB}_2) \quad \langle 1210 \rangle_{\text{MgB}_2} \parallel \langle 1210 \rangle_{\text{TiB}_2} (\text{AlB}_2)
\]
the rotation between the two matching planes (see Figure S7c,d), the possible orientation relationships between MgB$_2$ and TiB$_2$ (and/or AlB$_2$) are as follows:

\[
\begin{align*}
&\langle 10\bar{1}0 \rangle_{\text{MgB}_2} || \langle 10\bar{1}0 \rangle_{\text{TiB}_2 (\text{AlB}_2)} \quad \{0002\}_{\text{MgB}_2} \sim 0.03^\circ \text{ from } \{0002\}_{\text{TiB}_2 (\text{AlB}_2)} \\
&\langle \underline{1}2\underline{1}0 \rangle_{\text{MgB}_2} || \langle \underline{1}2\underline{1}0 \rangle_{\text{TiB}_2 (\text{AlB}_2)} \quad \{0002\}_{\text{MgB}_2} \sim 0.01^\circ \text{ from } \{0002\}_{\text{TiB}_2 (\text{AlB}_2)}
\end{align*}
\]

Table 4. The interatomic misfit along possible matching directions between MgB$_2$ and MB$_2$ (M = Ti or Al) nucleation center (%).

| MB$_2$/MB$_2$ | (\underline{1}2\underline{1}0) || (\underline{1}2\underline{1}0) | (\underline{1}2\underline{1}0) || (1\underline{0}1\underline{0}) | (\underline{1}0\underline{1}0) || (\underline{1}0\underline{1}0) | (\underline{1}0\underline{1}0) || (1\underline{0}0\underline{1}) |
|---------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| TiB$_2$       | 1.7                     | -70.3                   | 43.3                    | 1.7                     |
| AlB$_2$       | 2.6                     | -68.7                   | 43.8                    | 2.6                     |

3.5. Varied Morphology and Kinetics

As predicted, the heterogeneous nucleation of MgB$_2$ on Mg grains occurs along the directions $\langle 10\bar{1}0 \rangle_{\text{MgB}_2}$ and $\langle 0002 \rangle_{\text{MgB}_2}$. It is noted that the predicted orientation of MgB$_2$ agrees with our experimental observations on the morphology of the MgB$_2$ bars, as demonstrated in Figures 2 and 5. The subsequent growth dominantly along $\langle 12\underline{1}0 \rangle_{\text{MgB}_2}$ is likely due to the constrained growth along $\langle 0002 \rangle_{\text{MgB}_2}$ as well as $\langle 10\bar{1}0 \rangle_{\text{MgB}_2}$, both of which are in-plane directions at the MgB$_2$/Mg interface, resulting in a rectangular-shaped MgB$_2$ bar. Conversely, the growth of the MgB$_2$ platelets on TiB$_2$ nanoparticles is only limited along $\langle 0002 \rangle_{\text{MgB}_2}$, one of the in-plane directions at the MgB$_2$/TiB$_2$ interface. According to Figure 3, these MgB$_2$ platelets with a semi-circular shape are likely growing more randomly without a preferred growth direction.

The different MgB$_2$ morphologies, ranging from MgB$_2$ bars to MgB$_2$ platelets, are here ascribed to the different extent of the strain energy density induced at the interface to the nucleation center. Different aspect ratios of $\langle 12\underline{1}0 \rangle : \langle 10\bar{1}0 \rangle : \langle 0002 \rangle$ are determined to be about 50:5:1 for MgB$_2$ bars growing on Mg (Figure 2d), and about 15:1:5 for MgB$_2$ platelets growing on TiB$_2$ (Figure 3e). As the elastic-strain energy density $\epsilon$ is proportional to $Y\epsilon^2$, where $Y$ is Young’s modulus of MgB$_2$, and $\epsilon$ is the atomic misfit between MgB$_2$ and Mg or TiB$_2$, the strain energy density can be thus roughly estimated by the related misfits, by assuming constant $Y$ for simplicity. Along the interatomic direction $\langle 10\bar{1}0 \rangle_{\text{MgB}_2}$, the induced strain energy density is approximated to be more than 6 times larger for MgB$_2$ on Mg grains (misfit of 4.2%) than for MgB$_2$ on TiB$_2$ nanoparticles (misfit of 1.7%), as listed in Tables 2 and 4. Thus, the MgB$_2$ growth is hindered along the direction $\langle 10\bar{1}0 \rangle_{\text{MgB}_2}$ on Mg, leading to a lower aspect ratio $\langle 10\bar{1}0 \rangle : \langle 0002 \rangle$ of 5:1 for MgB$_2$ growth on Mg, compared with 15:1 for MgB$_2$ growth on TiB$_2$. The compelling growth restriction along $\langle 0002 \rangle$ can be also well-interpreted by the large interplanar misfit up to ~8% in both cases (Tables 1 and 3). Therefore, the difference in the elastic strain energy here is considered to be the root of the different MgB$_2$ morphologies, and furthermore, the changed desorption kinetic performances.

Figure 6 illustrates the complete process of the MgB$_2$ formation as discussed above. For MgB$_2$ growing on Mg grains, the further growth along $\langle 10\bar{1}0 \rangle_{\text{MgB}_2}$ is hampered due to a huge in-plane strain energy density, which forces itself to mainly grow in the out-of-plane direction $\langle 12\underline{1}0 \rangle_{\text{MgB}_2}$, ending up with these parallel-lying rectangular MgB$_2$ bars (Figure 6a). On the contrary, with an interatomic misfit of 1.7% between MgB$_2$ and TiB$_2$ along $\langle 10\bar{1}0 \rangle_{\text{MgB}_2}$, this in-plane growth constraint is not relevant (Figure 6b). The further growth of MgB$_2$ along the in-plane direction $\langle 10\bar{1}0 \rangle_{\text{MgB}_2}$ and the out-of-plane direction $\langle \underline{1}2\underline{1}0 \rangle_{\text{MgB}_2}$ can thus continuously proceed, leading to semi-circular shaped MgB$_2$ platelets. Furthermore, a critical value of the interatomic misfit between 1.7% and 4.2% may be
expected, above which the in-plane growth of MgB$_2$ is restricted. This may result in a deceleration of the MgB$_2$ nucleation and growth and, therefore, a decelerated desorption kinetics for the LiBH$_4$-MgH$_2$ composite.

As the growth of MgB$_2$ commonly leads to hexagonal plates [23], we speculate that the MgB$_2$ formation occurs at the interface between MgB$_2$ and its nucleation centers rather than on the MgB$_2$ surface exposed to the liquefied LiBH$_4$. This means that the formation of MgB$_2$ is always under the control of the in-plane strain energy density (Figure 6). From this perspective, the highly regular rectangular shape of the MgB$_2$ bars can be explained consistently. However, future in situ experiments are still required to confirm this speculation.

Figure 6. (a) Schematic illustration of how MgB$_2$ bars are generated based on Mg grains following a certain crystallographic orientation relationship. The nucleation and growth of MgB$_2$ may occur at the MgB$_2$/Mg interface under control of the in-plane strain energy density; (b) schematic illustration of the nucleation and growth of MgB$_2$ platelets based on TiB$_2$ nanoparticles at the MgB$_2$/TiB$_2$ interface.
4. Conclusions

Manifold TEM studies on the LiBH₄-MgH₂ composite with and without additives, combined with the predictions of the edge-to-edge matching model on the orientation relationship between the nucleation center and the resulting MgB₂ phase, contribute to a better understanding of the RHCs’ kinetics. According to this, the additives deliver a large number of nucleation centers with a small interatomic misfit of 1.7% to MgB₂, corresponding to low in-plane strain energy density. They facilitate the nucleation and growth of MgB₂, leading to the morphology of MgB₂ semi-circular platelets. In contrast, large in-plane strain energy density is expected for the formation of MgB₂ bars on Mg, limiting the growth of MgB₂ and consequently slowing down the dehydrogenation kinetics. To further improve the kinetic performance of the LiBH₄-MgH₂ composite, we suggest that the atomic misfit delivered by additives with respect to MgB₂ should be considered for future additive selection. It is also believed that these conclusions hold for other RHC systems interesting for hydrogen energy storage and release.

Supplementary Materials: The supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12111893/s1, Figure S1: The results of 2LiBH₄-MgH₂ without additives after desorption: STEM-HAADF image acquired from the corresponding position in Figure 2a and EDX elemental map of Mg; Figure S2: The results of 2LiBH₄-MgH₂ with 5 wt% 3TiCl₃·AlCl₃ after incomplete desorption: (a) STEM-HAADF image, and (b) the corresponding electron diffraction pattern; (c) STEM-HAADF image acquired from the selected area in (a) and (d) the corresponding EDX elemental map of Mg; Figure S3: The results of 2LiBH₄-MgH₂ with 0.625 mol% 3TiCl₃·AlCl₃ after desorption: (a) STEM-HAADF images showing the morphology of the generated MgB₂ crystals; (b) electron diffraction pattern; (c) STEM-HAADF image acquired from the corresponding position in (a), and EDX map of Mg; Figure S4: The results of 2LiBH₄-MgH₂ with 20 mol% 3TiCl₃·AlCl₃ after desorption: STEM-HAADF image acquired from the selected position in Figure 3a, and the corresponding EDX elemental map of Mg, Ti, and Al; Figure S5: The results of 2LiBH₄-MgH₂ with 20 mol% 3TiCl₃·AlCl₃ after desorption: HRTEM image acquired from the position of purple agglomerates in Figure 4a, and the corresponding FFT, showing the existence of TiB₂ (and AlB₂); Figure S6: The results of 2LiBH₄-MgH₂ with 20 mol% 3TiCl₃·AlCl₃ after desorption: (a) STEM-HAADF image showing the distribution of MgB₂ platelets; (b) electron diffraction patterns showing the crystallographic orientation of the corresponding MgB₂ platelets indicated in (a); Figure S7: Simulated superimposed diffraction patterns of MgB₂/Mg (a,b), and MgB₂/TiB₂ (c,d); Table S1: The interatomic misfit between (0002)ₘgB₂ and the possible matching directions of Mg nucleation center (%); Table S2: The interatomic misfit between (0002)ₘgB₂ and the possible matching directions of MB₂ (M = Ti or Al) nucleation center (%).

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