Reaction between LiBH_4 and MgH_2 Induced by High-Energy Ball Milling

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Abstract

Previous studies of *ab initio* density functional theory (DFT) calculations have predicted that reactions between LiBH_4 and MgH_2 can take place at temperature near 200°C. However, such predictions have been shown to be inconsistent with many experiments. Herein, we have designed a novel process termed as ball milling with aerosol spraying (BMAS) to prove, for the first time, that the reaction between LiBH_4 and MgH_2 can indeed occur during ball milling at room temperature. Through this BMAS process we have demonstrated unambiguously the formation of MgB_2 and LiH during ball milling of MgH_2 while aerosol spraying of the LiBH_4/THF solution. In this BMAS process, aerosol spraying of the LiBH_4/THF solution leads to the formation of LiBH_4 nanoparticles which decompose to form $\text{Li}_2\text{B}_{12}\text{H}_{12}$. The $\text{Li}_2\text{B}_{12}\text{H}_{12}$ formed then reacts with MgH_2 in situ during ball milling to form MgB_2 and LiH . The discovery made in this study has significant implications in making $\text{LiBH}_4 + \text{MgH}_2$ as a viable system for reversible hydrogen storage applications near ambient temperature in the future.

Keywords: Lithium borohydride; Magnesium hydride; Dehydrogenation; Hydrogen storage materials

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I. Introduction

Fuel cell technology is a valuable commodity because of the global demand for pollution-free energy systems. One indispensable component for successful fuel cell technology is to store hydrogen in a highly compacted manner for automobile on-board applications. In this context, the $\text{LiBH}_4 + \text{MgH}_2$ system has attracted worldwide attention recently because of its potential to store and release hydrogen at relatively low temperatures with a theoretical capacity of 11.6 wt.% H_2 [1-20]. The overall reaction for hydriding and dehydriding of the $\text{LiBH}_4 + \text{MgH}_2$ mixture (in a 2:1 molar ratio) has been generally agreed to be [1]

Furthermore, many studies [2-6,10] have revealed that the dehydrogenation process is actually composed of two elemental steps, i.e., MgH_2 decomposes into Mg and H_2 first, and then the newly formed Mg react with LiBH_4 to produce LiH , MgB_2 and H_2 , as indicated by the following two reactions [5]

As such, the onset temperature for releasing hydrogen from the $\text{LiBH}_4 + \text{MgH}_2$ system is controlled by the decomposition temperature of MgH_2 . Moreover, the decomposition of MgH_2 has a reaction enthalpy of ~ 76 kJ/mol H_2 [21], and therefore the temperature for MgH_2 to have a hydrogen equilibrium pressure of 1.0 bar is approximately 311°C (585 K). This theoretical consideration is consistent with the observation that temperatures in excess of 300°C are normally required to obtain noticeable decomposition of MgH_2 in the pure form [22-26] and in the $2\text{LiBH}_4 + \text{MgH}_2$ mixture [2,5-7,10]. Thus, in spite of the fact that reaction (1) possesses favorable thermodynamic property with a desorption enthalpy of ~ 46 kJ/mol H_2 [1], the utilization of reaction (1) is limited by the onset temperature for MgH_2 to release hydrogen substantially.

Recently, *ab initio* density functional theory (DFT) calculations [27,28] have predicted that the hydrogen release process of LiBH_4 involves the formation of an intermediate, $\text{Li}_2\text{B}_{12}\text{H}_{12}$, as shown in reaction (4).

This reaction can theoretically result in release of 10 wt% H₂ and its standard reaction enthalpy of has been calculated to be 44.4 kJ/mol H₂ [28], suggesting that hydrogen release of LiBH₄ can take place at ~170°C and ~48°C when the hydrogen equilibrium pressure is at 1.0 and 0.01 bar, respectively. Experimentally, Li₂B₁₂H₁₂ has been confirmed as one of the desorption products of LiBH₄ [29-33], but often formed at high temperatures, such as 427–457°C [29], indicating a significant kinetic barrier for the formation of Li₂B₁₂H₁₂.

The *ab initio* DFT calculation [28] also predicts that Li₂B₁₂H₁₂ can react with MgH₂, as shown in reaction (5) below. This reaction has been predicted to have the standard reaction enthalpy and entropy of 60.1 kJ/mol H₂ and 123.3 J/k mol H₂, respectively, and thus has favorable thermodynamics for reversible hydrogen storage at 214°C and 98°C when the hydrogen equilibrium pressure is 1.0 and 0.01 bar, respectively. However, this reaction has not been observed at these predicted temperatures because no one can form the reactant Li₂B₁₂H₁₂ at such low temperatures.

Inspired by these first-principles calculations [27,28], we have recently investigated the possibility of releasing hydrogen from nanoscale LiBH₄ particles via reaction (4) near room temperature [34]. We have developed an approach based on the evaporation of the solvent from a LiBH₄-containing solution [34] to produce nanoscale LiBH₄ particles which have been shown to release H₂ at temperatures as low as 32°C, very close to the theoretical calculation of 48°C [28]. Furthermore, these nanoscale LiBH₄ particles can reversibly release and uptake 1.85 wt% H₂ at 265°C with the formation of Li₂B₁₂H₁₂ at 265°C or lower, confirming that reaction (4) can indeed take place below 265°C as predicted by the *ab initio* DFT calculation [28]. It is further shown that the improved thermodynamic driving force and reaction kinetics are the reasons why nanoscale LiBH₄ can form Li₂B₁₂H₁₂ at low temperatures while coarse LiBH₄ particles cannot [34].

In this article, we show, for the first time, that reaction between LiBH₄ and MgH₂ can occur during high-energy ball milling at ambient temperature. The XRD and FTIR analyses reveal that the reaction between LiBH₄ and MgH₂ proceeds via Eqs. (4) and (5). These results confirm, for the first time, that reactions (4) and (5) can indeed take place at much lower temperatures than 400°C, as predicted by the *ab initio* DFT calculations [27,28]. These findings provide a new direction for future investigations in designing nanostructured LiBH₄ and MgH₂ mixtures to attain hydrogen uptake and release near ambient temperature.

II. Materials and Procedure

MgH₂ powder of 98% purity and 2M LiBH₄ in tetrahydrofuran (2M LiBH₄/THF) solution were purchased from Sigma-Aldrich without pretreatment. It has been proved that the presence of graphite can not only offer effective and uniform mixing, but also enhance dehydrating prosperities of MgH₂ [22-24,35-37]. Therefore, synthetic graphite (C) powder (Sigma-Aldrich) was purchased and pre-milled for 6 h at room temperature under an argon atmosphere in the SPEX ball milling machine in order to reduce to the particle size of graphite before mixing with MgH₂. The pre-milled graphite was then mixed with MgH₂ at an amount of 6 wt.% (i.e., 5 vol.%) of the total MgH₂ + C mixture.

The MgH₂ + C mixture was ball milled for 3 h, 6 h and 12 h with continuous aerosol spraying of the 2M LiBH₄/THF solution into the canister during ball milling. This process will be termed as ball milling with aerosol spraying (BMAS) hereafter. The schematic of the BMAS device is shown in Figure 1. Basically, it consists of a modified Szegvari attritor, which is effective in preventing the formation of dead zone during ball milling and producing uniform milling products within the powder charge [8,12,18,38-43]. The nozzle of the aerosol generator is installed at the top of the canister and its on-and-off operation can be controlled independently from the ball milling operation of the attritor. The aerosol generator was purchased from TSI instrument with capability to produce nanoparticles with sizes ranging from 0.02 to 0.30 micrometers, depending on the spraying conditions.

In the BMAS process, aerosol droplets of the 2M LiBH₄/THF solution are sprayed into the air-tight canister of the attritor, while high-energy ball milling of the MgH₂ + C particles is taking place. Aerosol liquid droplets will become solid nanoparticles when the droplets impinge on the surfaces of MgH₂ particles and balls where the local temperature can be as high as 200 - 250 °C due to the high-speed collision of balls [12,44,45]. Since the boiling temperature of THF is only 66 °C, it is expected that the high local temperature will force THF solution to vaporize instantaneously, leading to the formation of solid LiBH₄ nanoparticles. As a result, nano-LiBH₄ will coat on the surface of MgH₂ particles first, and be occluded into MgH₂ nanoparticles later as ball milling continues, owing to repeated fracture and cold-welding of MgH₂ particles during ball milling. A vacuum pump is connected to one of the relief valves of the canister to maintain the gas pressure of the canister so that vaporization of the THF solvent from aerosols can proceed as desired.

The canister of the attritor and the balls (6.4 mm in diameter) were made of stainless steel. The loading of the powder mixture and balls to the canister was performed in a glove-box filled with ultrahigh-purity argon (99.98%). The ball-to-powder weight ratio was 60:1, the milling speed was 600 rpm, the milling temperature was maintained at 20 °C for 3h and 6h operations, achieved by water-cooling around the canister at a flowing rate of 800 ml/min. However, for 12h ball milling no water-cooling was implemented. Thus, the average temperature of the canister was measured to be about 95 °C

due to the heat generated by ball collision (see Figure S1 in Supplementary Materials). Table 1 lists sample IDs and their processing conditions.

The $\text{MgH}_2 + \text{C}$ mixtures with and without aerosol spraying during ball milling were analyzed using a D2 PHASER X-ray diffractometer (XRD). The operation conditions for the XRD data collection were $\text{CuK}\alpha$ radiation, 40 kV, 40 mA, 0.03 °/min, and 0.02 °/step. To prevent oxidation during XRD data collection, the sample was sealed in a capillary quartz tube of 1.5 mm in diameter and the loading of the sample to the tube was performed in a glove box filled with Ar. The wall of the capillary quartz tube is 0.01 mm in thickness and thus transparent to X-ray. 325-mesh pure silicon powder was added at 10 wt.% to the ball milled powders as an internal standard for accurate identification of peak positions. The coarse-grained silicon powder was also used to correct for instrumental broadening, so that the Scherrer formula [46] could be used to estimate crystallite sizes for MgH_2 from the (101) reflection. The addition of 10 wt.% Si in each sample as the internal standard was also utilized to quantify the amount of LiBH_4 in the BMAS-processed samples. This was carried out with the aid of the following equation [8,46]

$$\frac{I_i}{I_{Si}} = \frac{K_i}{K_{Si}} \frac{V_i}{V_{Si}} = \left(\frac{K_i}{K_{Si}} \frac{\rho_{Si}}{w_{Si} \rho_i} \right) w_i \quad (6)$$

where subscripts i and Si stand for the i th phase and Si phase in the powder mixture respectively, I is the integrated intensity, V is the volume fraction, w is the weight fraction, ρ is the density, and K is a parameter related to the structure factor, intensity of the incident beam, total volume of the diffracting crystals, multiplicity of the reflecting planes, and other experimental factors. K can be further described as $K_i = K_{i\text{-const}} \times V_i$ where V_i is the total volume of the i th phase (the diffracting crystal) and $K_{i\text{-const}}$ is a XRD parameter *independent* of the quantity of the i th phase in the powder mixture [46]. The use of Eq. (6) to quantify the amount of LiBH_4 in the BMAS-processed samples is detailed in the appendix.

Fourier transform infrared (FTIR) analysis (Nicolet, Nexus-IR 470) was conducted on the BMAS-processed samples in order to check if LiBH_4 was successfully coated on the MgH_2 particles during ball milling. Around 1 wt% BMAS-processed powder was mixed and ground with KBr powder in a glovebox filled with Ar of 99.98% purity. The ground mixture was subsequently pressed into a pellet 1 cm in diameter in air very quickly (~30 s) in order to avoid excessive oxidation. Although the hydride powder on the pellet surface was oxidized, the hydride powder in the interior was not because of the protection from 99 wt % KBr powder in the mixture. Prior to the collection of each spectrum, the background of air was measured and subtracted from the result.

To ensure that the aerosol spraying generator is working properly, the particles produced from aerosol spraying of the LiBH_4/THF solution was collected using a porous polytetrafluoroethylene (PTFE)

membrane (rather than spraying into the ball milling canister directly) and examined using a scanning electron microscope (SEM, JEOL JSM-6335F). The LiBH_4 particles trapped by the porous PTFE membrane were coated with gold in 2.2kV voltage and 20 mA current for 2 minutes using an E5100 SEM COATING UNIT from Polaron Instrument Inc. before SEM examination.

III. Results and Discussion

To ensure the aerosol generator can produce LiBH_4 particles with sizes in 20 to 100 nm, we have sprayed LiBH_4/THF solution to a porous PTFE membrane and examined the morphology and size of the particles trapped by the PTFE membrane using SEM. The result confirms that aerosol sprayed LiBH_4 particles are indeed in the range of 20 to 100 nm (see Figure S2). Thus, when sprayed into a ball milling canister, these LiBH_4 nanoparticles are expected to be occluded into MgH_2 nanoparticles because of repeated fracture and cold welding of MgH_2 during ball milling, thereby creating a uniform mixture of MgH_2 and LiBH_4 at nanoscales.

Figure 2 summarizes the XRD patterns of the $\text{MgH}_2 + 5 \text{ vol.}\% \text{ C}$ mixtures under different ball milling conditions. Samples with ball milling but without aerosol spraying of the LiBH_4/THF solution (Figures 2a and 2f) are also included as the references for comparison with those with aerosol spraying (Figures 2b, 2c, 2d and 2e), while the XRD pattern of the $\text{MgH}_2 + 5 \text{ vol.}\% \text{ C}$ mixture without ball milling is shown in Figure S3. Several interesting phenomena are noted from these XRD patterns. First, the XRD pattern of the $\text{MgH}_2 + 5 \text{ vol.}\% \text{ C}$ mixture without ball milling (Figure S3) matches the MgH_2 standard (04-013-2314) well and no MgO is present. However, there are trace amounts of impurities, as evidenced by two un-identified peaks located at $\sim 32^\circ$ and 37° . The broad peak at $\sim 25^\circ$ is due to the capillary tube because the XRD pattern of the capillary tube exhibits this peak. Second, XRD spectra of all ball milled samples exhibit the peaks of MgH_2 clearly, indicating that ball milling has been conducted with little or no oxidation. Third, the integrated peak intensities of MgH_2 decrease with increasing the ball milling duration, suggesting that the addition of LiBH_4 via aerosol spraying has taken place during ball milling. Fourth, broadening of MgH_2 peaks has occurred, suggesting crystallite size refinement and/or introduction of structural defects into crystalline MgH_2 during the ball milling process.

Using the Scherrer formula and taking the broadening of MgH_2 (101) peak, the crystallite size of MgH_2 for each ball milling condition has been estimated. Using Eq. (6-4) in the appendix and the integrated intensities of Si (220) and MgH_2 (101) peaks, the weight percentage of MgH_2 in the $\text{MgH}_2 + \text{C} + \text{LiBH}_4$ mixture as a function of aerosol spraying conditions has been computed. These results are presented in Table 2. It can be seen from Table 2 that the crystallite sizes of MgH_2 are estimated to be ~ 25 nm or lower for the $\text{MgH}_2 + \text{C}$ mixtures ball milled with the average temperature at 25°C for 3, 6 and 12 h

with or without aerosol spraying. This is consistent with a previous study [12] showing that ball milling for 5 h leads to formation of nanocrystalline MgH_2 (66 nm). However, when ball milling is conducted with the average temperature at 95°C (sample MCA-12A), the crystallite size becomes ~ 150 nm. The larger crystallite size derived from higher average ball milling temperature is consistent with the expectation because higher ball milling temperature will lead to faster crystallite growth and thus larger crystallite sizes.

Another important set of data in Table 2 is the weight percentages of MgH_2 in the $\text{MgH}_2 + \text{C} + \text{LiBH}_4$ mixtures which decrease with increasing the aerosol spraying time. This is consistent with the expectation that more and more LiBH_4 is added to the mixture as the aerosol spraying time increases. When the weight percentage of MgH_2 in the mixture is plotted as a function of the aerosol spraying time (Figure 3), it is noted that the quantity of MgH_2 is decreased linearly with the ball milling time when the average ball milling temperature is kept constant at 25°C . However, when the average ball milling temperature is changed to 95°C (MCA-12A with no water cooling during ball milling), the quantity of MgH_2 decreases faster than the expected linear reduction. We have ascribed the accelerated MgH_2 decrease of MCA-12A to two simultaneous processes: one being the linear addition of LiBH_4 due to aerosol spraying and the other due to the reaction of MgH_2 with $\text{Li}_2\text{B}_{12}\text{H}_{12}$ according to reactions (4) and (5). The $\text{Li}_2\text{B}_{12}\text{H}_{12}$ comes from the decomposition of the nanoscale LiBH_4 generated via aerosol spraying and instant vaporization of the THF solvent during ball milling. As pointed out previously, we have shown that nanoscale LiBH_4 can release hydrogen via reaction (4) near room temperature [34].

To further confirm the occurrence of reactions (4) and (5) during ball milling, we have examined the XRD pattern of each aerosol sprayed sample in detail to see whether there are MgB_2 and LiH in the sample. The presence of MgB_2 is expected if reaction (5) has indeed taken place during ball milling. The strongest peak of MgB_2 is from (101) planes and located at 42.37° ; the second strongest peak of MgB_2 is from (110) planes and located at 59.81° , while the third strongest peak is from (102) planes and present at 63.13° . Therefore, we have focused on the XRD pattern at the 2-theta range from 39° to 45° (the strongest peak position) and from 58° to 64° (the second strongest peak position). Figure 4(a) and (c) show the comparison of the XRD patterns of MCA-12A with the standard MgB_2 (04-014-0070), MgH_2 (04-013-2314) and MgO (01-075-9568) XRD patterns in these two 2-theta ranges. We note that MgO peaks are also present at these two 2-theta ranges with the strongest peak from (200) planes at 42.17° and the second strongest peak from (220) planes at 61.17° . Therefore, we have included MgO in the analysis. Since there are three possible phases in these 2-theta ranges, we have carried out de-convolution of the XRD spectrum into 3 phases (MgH_2 , MgB_2 and MgO). In the curve fitting through the de-convolution analysis, we have fixed the peak position of MgH_2 , MgB_2 and MgO according to their standards MgH_2 (04-013-2314), MgB_2 (04-014-0070) and MgO (01-075-9568), respectively. The peak intensity is the

only variable in the curve fitting and the outcome with the minimum error between the fitting data and experimental spectrum is taken as the final result. Figure 4(b) and (d) show the curve fitting results and Table 3 summarizes the integrated area of each phase from the curve fitting. This analysis unambiguously reveals the formation of MgB_2 and MgO in MCA-12A.

The same XRD peak analysis for MCA-12A is also applied to the MCA-3, MCA-6 and MCA-12B samples. The results are shown in Figures 5, 6 and S4. It is interesting to note that all MCA-3, MCA-6 and MCA-12B samples do not contain MgO or its content is so small that it cannot be detected (see Figures 5b, 5d, 6b and Figure S4). These samples also contain lower integrated area of MgB_2 than MCA-12A does, as shown in Table 3. Moreover, the quantities of MgB_2 in MCA-3, MCA-6 and MCA-12B are so small that the second strongest peak of MgB_2 located at 59.81° does not appear at all (Figure S4 and Table 3). In addition, the MgH_2 peak at 61.37° does not appear for all ball milled samples (Figures 2, 4d, S4, and Table 3). We attribute this phenomenon to the weak intensity of the MgH_2 peak at 61.37° (Figure S3) along with intensive ball milling because intensive high-energy ball milling can often result in weak peaks of nanocrystalline materials to disappear [39-41].

The presence of a small amount of MgO in MCA-12A is ascribed to a trace amount of impurities in the argon atmosphere. In contrast, no MgO in the MCA-3, MCA-6 and MCA-12B is due to their lower average ball milling temperature (with water cooling during ball milling), while MCA-12A is ball milled without water cooling. The lower average ball milling temperature for MCA-3, MCA-6 and MCA-12B can presumably suppress the oxidation of MgH_2 by the trace amount of impurities in the argon atmosphere.

It should be pointed out that there are two possible ways to form MgB_2 during high-energy ball milling of MgH_2 with the assistance of aerosol spraying of the LiBH_4/THF solution. One very unlikely way is through reaction (1). As mentioned before, this reaction proceeds by two elemental steps, first reaction (2) and then reaction (3) [2-6,10]. However, high-energy ball milling of MgH_2 at ambient temperature without water cooling has been studied by many groups, and no decomposition of MgH_2 during ball milling, i.e. reaction (2), has ever been reported [22-26,47-49]. The present study also confirms that this is indeed the case. As shown in Figure 2, the XRD patterns of $\text{MgH}_2 + 5 \text{ vol.}\% \text{ C}$ ball milled for 3 h with water cooling (MC-3) and 12 h without water cooling (MC-12) do not exhibit the formation of Mg , indicating that reaction (2) cannot occur during high-energy ball milling with or without water cooling. Furthermore, high-energy ball milling of $\text{MgH}_2 + \text{LiBH}_4$ mixtures at ambient temperature without water cooling has also been investigated by a large number of researchers, and no formation of MgB_2 has been reported [6,11-13,17-20]. Therefore, reaction (1) cannot be induced by high-energy ball milling at ambient temperature since it has never been reported to occur during high-energy ball milling [6,11-13,17-20].

Since reaction (1) cannot be induced by high-energy ball milling at ambient temperature, we propose that the formation of MgB_2 during the BMAS process is through reactions (4) and (5). Previous studies [44,45] have indicated that the local temperature at the collision site during high-energy ball milling is $200^\circ\text{C} - 250^\circ\text{C}$ higher than the average ball milling temperature of the canister [44,45]. This temperature spike at the collision site is in a very short duration (of the order of $10^{-6} - 10^{-5}$ s) during high-energy ball milling [44,45]. Although this temperature spike is not enough to induce the decomposition of MgH_2 [22-26,47-49] and the reaction between MgH_2 and LiBH_4 during high-energy ball milling [6,11-13,17-20], this temperature spike is sufficient to induce reactions (4) and (5) during the BMAS process. Specifically, our previous study [34] has shown that the nanoscale LiBH_4 particles produced via evaporation of the THF solvent from the LiBH_4/THF solution can release H_2 at temperatures below 50°C via reaction (4). The $\text{Li}_2\text{B}_{12}\text{H}_{12}$ product from reaction (4) can then react with MgH_2 via reaction (5) during ball milling because the local temperature spike at the collision site is 200 to 250°C higher than the average temperature of the canister. It is this temperature spike that results in the occurrence of reactions (4) and (5). However, this temperature spike is not enough to trigger reactions (2) and (3), as shown by numerous studies [6,11-13,17-20, 22-26,47-49].

The occurrence of reaction (5) during the BMAS process is consistent with the *ab initio* DFT calculation [28] predicting that reaction (5) has favorable thermodynamics for reversible hydrogen storage at 214°C and 98°C when the hydrogen equilibrium pressure is 1.0 and 0.01 bar, respectively. Reaction (5), however, has never been observed by other researchers because $\text{Li}_2\text{B}_{12}\text{H}_{12}$ needs to be formed via decomposition of coarse-grained LiBH_4 at temperatures as high as $427 - 457^\circ\text{C}$ [29-33]. Reaction (5) becomes possible in this study because the nanoscale LiBH_4 can decompose to form $\text{Li}_2\text{B}_{12}\text{H}_{12}$ at temperatures below 50°C [34] and the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ formed can then react with MgH_2 gradually during high-energy ball milling. The MCA-12A sample contains much higher MgB_2 contents than MCA-3, MCA-6 and MCA-12B because the former does not have water cooling during the BMAS process and thus has higher local temperatures at the collision site during ball milling ($\sim 75^\circ\text{C}$ higher).

If reactions (4) and (5) indeed take place, one also expects to find the evidence of LiH and $\text{Li}_2\text{B}_{12}\text{H}_{12}$ because $\text{Li}_2\text{B}_{12}\text{H}_{12}$ is an intermediate (Eq. 4) and LiH is the final product (Eq. 5). LiH peaks, however, are not obvious in the XRD patterns because the intensities of LiH peaks are very low in comparison with that of MgB_2 and Si peaks [8]. Therefore, no obvious LiH peak in the BMAS-processed samples is consistent with our expectation. For $\text{Li}_2\text{B}_{12}\text{H}_{12}$, the strongest and second strongest peaks should be present at 16.2° and 18.5° [50], respectively, but they are overlapped with the peak from the capillary glass tube. Thus, the FTIR analysis has been conducted since $\text{Li}_2\text{B}_{12}\text{H}_{12}$ can also be identified via FTIR analysis [34,50].

Figures 7 and 8 summarize the FTIR spectra of BMAS-processed samples with different ball milling temperatures and times. It is very clear from Figure 8 that all BMAS-processed samples have the characteristic absorption peaks of LiBH_4 at 2387, 2292 and 2225 cm^{-1} , which are very close to the characteristic absorption frequencies of commercially purchased bulk LiBH_4 powder at 2384, 2292, and 2225 cm^{-1} (Figure S5). The characteristic absorption peak of LiBH_4 at 1126 cm^{-1} (Figure S5) is also present for all BMAS-processed samples (Figure 7). Therefore, it can be concluded that LiBH_4 has been formed during high-energy ball milling of MgH_2 with aerosol spraying of the LiBH_4/THF solution. The presence of LiBH_4 in the ball milled samples also indicates that the LiBH_4 generated from aerosol spraying of the LiBH_4/THF solution has not completely reacted with MgH_2 during ball milling yet.

Equally important, Figure 7 shows the presence of LiH , as evidenced by its characteristic absorption peak at 1030 cm^{-1} [51], confirming the occurrence of reactions (4) or (5) or both since we have already ruled out the possibility of reactions (2) and (3). However, combining this evidence with the evidence of MgB_2 in the final products for all BMAS-processed samples (Table 3), one can conclude safely and unambiguously that reaction (5) has taken place during high-energy ball milling of MgH_2 with aerosol spraying of the LiBH_4/THF solution. This result is in good accordance with the prediction of the DFT calculations [27,28] and a previous experimental study [34] showing that reaction (4) can take place near the ambient temperature for the nanoscale LiBH_4 generated from LiBH_4/THF solution. The occurrence of reaction (4) results in $\text{Li}_2\text{B}_{12}\text{H}_{12}$ which can then allow reaction (5) to take place during high-energy ball milling.

It should be emphasized that high-energy ball milling of micron-sized LiBH_4 and MgH_2 mixtures has been conducted before [6,11-13,17-20]. However, no reactions between micron-sized LiBH_4 and MgH_2 have been reported. Therefore, the formation of MgB_2 and LiH in the present study is due to the novel process of ball milling with aerosol spraying developed in this study. Aerosol spraying of the LiBH_4/THF solution leads to the formation of LiBH_4 nanoparticles which can then decompose to form $\text{Li}_2\text{B}_{12}\text{H}_{12}$ according to reaction (4). The $\text{Li}_2\text{B}_{12}\text{H}_{12}$ formed can then react with MgH_2 in situ during ball milling according to reaction (5). The collision of balls during high-energy ball milling results in temperature spike locally to offer the required temperature (200 to 250°C) for reactions (4) and (5) to take place at and near the collision site.

It is noted that Figures 7 and 8 also provide several other interesting phenomena. First, by comparing the FTIR spectra of $\text{MgH}_2 + 5 \text{ vol.}\% \text{ C}$ without ball milling with the BMAS-processed samples (i.e., curve *d* versus curves *a*, *b* and *c* in Figure 7), it can be concluded that there are un-reacted MgH_2 in all BMAS-processed samples, as evidenced by the presence of a broad absorption peak at ~600 cm^{-1} and those ranging from 900 to 1300 cm^{-1} [12], overlapped with the characteristics absorption peaks of LiBH_4 at 1126 cm^{-1} and LiH at 1030 cm^{-1} . Second, moisture peaks at 3448 and 1640 cm^{-1} are present in

all samples (Figure 7). We attribute the presence of moisture to short exposure to air during the FTIR sample preparation (~30 s) since the commercially purchased bulk LiBH_4 , MgH_2 and KBr powders, prepared in the same way as the BMAS-processed samples for the FTIR analysis, also contain these moisture absorption peaks (Figures 7, S5 and S6). It should be pointed out that if the BMAS process were contaminated with moisture, one would have expected the following hydrolysis reaction [52] to take place because LiBH_4 is much more sensitive to water than MgH_2 . This reaction will lead to the formation of LiBO_2 owing to its large negative Gibbs free energy of formation [52].

However, by comparing Figures 7 (BMAS-processed samples) and S7 (LiBO_2 sample), it is clear that the absorption peaks of LiBO_2 at 1400 cm^{-1} and 680 cm^{-1} are absent from our BMAS-processed samples, and thus there is no evidence of moisture contamination in our BMAS process. In contrast, the evidence of the presence of LiBH_4 in the BMAS-processed samples is unequivocal (Figure 8), indicating that LiBH_4 is not oxidized during ball milling.

Other phenomena that can be observed from Figures 7 and 8 are the presence of two characteristic absorption peaks of CO_2 in all samples at 2060 and 2349 cm^{-1} [51]. This phenomenon is also attributed to short exposure to air during the FTIR sample preparation, which results in absorption of CO_2 on the surface of the samples and surface oxidation of nano-graphite particles when the samples contain carbon (such as the BMAS-processed samples). This argument is supported by the fact that (i) the absorption peaks of CO_2 are present in the commercial KBr sample (spectrum *e* in Figure 8), and (ii) these peak intensities increase when the samples contain carbon (spectra *a*, *b*, *c* and *d* in Figure 8). We also notice the presence of three characteristic absorption peaks of the C-H bond at 2863 , 2900 and 2966 cm^{-1} [51]. This C-H bond is likely due to slight organic contamination from the commercially purchased bulk KBr powder (Figure S6). However, it should be pointed out that the two characteristic absorption peaks of THF are also present in this region (at 2850 and 2950 cm^{-1}) [51] and thus can overlap with the absorption peaks of the C-H bond. According to Figure 7, the two peaks near 2850 and 2950 cm^{-1} increase with the aerosol spraying time (from MCA-3 to MCA-6), but decrease for MCA-12A. Such changes may be interpreted as the result of changing the average ball milling temperature. When the average ball milling temperature increases from 25°C (MCA-3 and MCA-6) to 95°C (MCA-12A), THF becomes easier to remove through vaporization during ball milling. As shown in Figure S8, THF can vaporizes completely in the 20-min holding at room temperature because its boiling temperature is 66°C . However, when THF is used as a solvent to dissolve LiBH_4 , evaporation of THF becomes much slower. Nevertheless, our previous study [34] has shown that the THF residual in the LiBH_4/THF powder could

be removed completely under a vacuum of 10^{-4} MPa at room temperature for 36 h. Finally, the characteristic B-H stretching vibration from $\text{Li}_2\text{B}_{12}\text{H}_{12}$ at 2479 cm^{-1} [34,53] is not noticeable (Figure 8). We attribute this result partially to the intrinsic nature of the weak peak of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ at 2479 cm^{-1} in comparison with the strong peaks of LiBH_4 at 2387, 2292 and 2225 cm^{-1} [34]. The in-situ reaction of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ with MgH_2 during high-energy ball milling to form MgB_2 and LiH according to reaction (5) can also result in little or no $\text{Li}_2\text{B}_{12}\text{H}_{12}$ in the final powder product.

IV. Conclusions

In this study we have developed a novel process termed as ball milling with aerosol spraying (BMAS) to enable the reaction between LiBH_4 and MgH_2 during high-energy ball milling with or without water cooling. We have demonstrated, for the first time, that formation of MgB_2 and LiH from the reaction between LiBH_4 and MgH_2 is achievable via ball milling of $\text{MgH}_2 + 5\text{ vol\% C}$ mixture along with in-situ aerosol spraying of the LiBH_4/THF solution. Aerosol spraying of the LiBH_4/THF solution leads to the formation of LiBH_4 nanoparticles which can then decompose to form $\text{Li}_2\text{B}_{12}\text{H}_{12}$ according to reaction (4). The $\text{Li}_2\text{B}_{12}\text{H}_{12}$ formed can then react with MgH_2 in situ during ball milling according to reaction (5). The collision of balls during high-energy ball milling at ambient temperature results in temperature spike locally to offer the required temperature (200 to 250°C) for reactions (4) and (5) to take place at and near the collision site. This is the first time that reactions (4) and (5) predicted by the DFT calculations [27,28] are proven to occur during ball milling with the average ball milling temperature at either 25°C or 95°C . Ball milling at 95°C (air cooling) induces more reactions between LiBH_4 and MgH_2 than ball milling at 25°C (water cooling).

Finally, it should be pointed out that the BMAS process can be utilized in the future to synthesize nanoscale $\text{MgH}_2 + \text{LiBH}_4$ mixtures without reactions between them if the BMAS process can be carried out at temperatures lower than the ambient to suppress reactions (4) and (5) during ball milling. Should such a modified BMAS is achieved, the nanoscale $\text{MgH}_2 + \text{LiBH}_4$ mixtures produced can then release and uptake H_2 according to reactions (4) and (5) near ambient temperature. Such a study is currently ongoing and the result will be published in a future article.

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Appendix: Quantification of Phases using XRD with a Si Internal Standard

The addition of 10 wt.% Si in each sample as the internal standard can be utilized to quantify the amount of the phase(s) in the BMAS-processed samples. This is carried out with the aid of the following equation [8,46]

$$\frac{I_i}{I_{Si}} = \frac{K_i}{K_{Si}} \frac{v_i}{v_{Si}} = \left(\frac{K_i}{K_{Si}} \frac{\rho_{Si}}{w_{Si} \rho_i} \right) w_i \quad (6)$$

To utilize Eq. (6), the following steps have to be taken. First, take the XRD pattern of the ball milled MgH₂ (without aerosol spraying of LiBH₄/THF solution) plus 10 wt.% Si sample and get the integrated intensities of MgH₂ (101) peak and Si (220) peak. Denoting them as I_{MgH₂} and I_{Si}, respectively and inserting them into Eq. (6), one has

$$\frac{I_{MgH\ 2}}{I_{Si}} = \frac{K_{MgH\ 2-const}}{K_{Si-const}} \frac{V_{MgH\ 2} v_{MgH\ 2}}{V_{Si} v_{Si}} = \left(\frac{K_{MgH\ 2-const}}{K_{Si-const}} \frac{\rho_{Si}^2}{W_{Si}^2 \rho_{MgH\ 2}^2} \right) W_{MgH\ 2}^2 \quad (6-1)$$

where W_i is the total weight of the *i*th phase in the powder mixture. Note that K_{MgH₂-const} is normally unknown, but depends on the MgH₂ phase properties only, not its quantity. The same is true for K_{Si-const}. Selection of MgH₂ (101) peak and Si (220) peak for analysis is due to the fact that they are strong peaks with no overlapping with other peaks.

Second, take the XRD pattern of the LiBH₄-sprayed MgH₂ plus 10 wt.% Si sample and get the integrated intensities of MgH₂ (101) peak and Si (220) peak. Denoting them as I'_{MgH₂} and I'_{Si}, respectively and inserting them into Eq. (6), one has

$$\frac{I'_{Li\ 2S}}{I'_{Si}} = \frac{K_{MgH\ 2-const}}{K_{Si-const}} \frac{V'_{MgH\ 2} v'_{MgH\ 2}}{V'_{Si} v'_{Si}} = \left(\frac{K_{MgH\ 2-const}}{K_{Si-const}} \frac{\rho_{Si}^2}{W_{Si}^2 \rho_{MgH\ 2}^2} \right) W'^2_{MgH\ 2} \quad (6-2)$$

Dividing Eq. (6-1) by Eq. (6-2), one has

$$\frac{I_{MgH\ 2}}{I_{Si}} / \frac{I'_{MgH\ 2}}{I'_{Si}} = W_{MgH\ 2}^2 / W'^2_{MgH\ 2} \quad (6-3)$$

Eq. (6-3) can be converted to

$$\frac{I_{MgH_2}}{I_{Si}} / \frac{I'_{MgH_2}}{I'_{Si}} = w_{MgH_2}^2 / w'^2_{MgH_2} \quad (6-4)$$

If and only if the total powder mixture weight of the ball milled $MgH_2 + 10 \text{ wt.}\%$ Si sample is the same as that of the $LiBH_4$ -sprayed $MgH_2 + 10 \text{ wt.}\%$ Si sample.

Since we know every parameter in the left-hand side of Eq. (6-4) and w_{MgH_2} equals to 84 wt.% (due to the addition of 10 wt.% Si and the presence of 6 wt.% graphite in the powder mixture), we can calculate w'_{MgH_2} . Note that w'_{MgH_2} will be smaller than 84 wt.% because of the presence of the $LiBH_4$ spraying. Table 2 summarizes the integrated intensities of Si (220) and MgH_2 (101) for various samples along with the calculated MgH_2 quantities using Eq. (6-4).

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Tables and Figures

Table 1. Sample synthesis and processing conditions

Sample ID	Composition*	Ball milling time / average temperature
MC-3	MgH ₂ + C	3h / 25°C
MCA-3	MgH ₂ + C + AS	3h / 25°C
MCA-6	MgH ₂ + C + AS	6h / 25°C
MCA-12A	MgH ₂ + C + AS	12h / 95°C
MCA-12B	MgH ₂ + C + AS	12h / 25°C
MC-12	MgH ₂ + C	12h / 95°C

* AS stands for aerosol spraying of LiBH₄/THF solution during ball milling

Table 2. Integrated intensities, crystallite sizes and quantity of MgH₂ from XRD analysis

Sample ID	Integrated intensity of Si (220)	Integrated intensity of MgH ₂ (101)	Crystallite size of MgH ₂ (nm)	Quantity of MgH ₂ (wt%)
MC-3	3455	3029	12.01	94.0
MCA-3	3552	2939	13.91	91.3
MCA-6	3052	2347	18.82	88.0
MCA-12A	2792	987	148.59	59.7
MCA-12B	3069	2010	26.68	81.2

Table 3. The integrated area of each peak derived from de-convolution of the XRD spectrum indicated*

Sample ID	2-theta range (39° – 45°)			2-theta range (58° – 64°)		
	MgB ₂	MgH ₂	MgO	MgB ₂	MgH ₂	MgO
MC-3	None	D	N/D	None	N/D	N/D
MCA-3	0.60	0.72	N/D	N/D	N/D	N/D
MCA-6	0.72	0.52	N/D	N/D	N/D	N/D
MCA-12A	2.38	0.41	2.22	1.46	N/D	1.30
MCA-12B	D	D	N/D	N/D	N/D	N/D

* N/D stands for “not detectable” and D means “detected”.

Figure 1. Schematic of the device for the ball milling with aerosol spraying (BMAS) process in making nano-particles with reactants LiBH_4 and MgH_2 mixing at the nanometer scale.

Figure 2. X-ray diffraction patterns of $\text{MgH}_2 + 5 \text{ vol.\% C}$ mixtures: (a) ball milled at room temperature for 3h without aerosol spraying (MC-3 in Table 1); (b) ball milled at room temperature with aerosol spraying for 3h (MCA-3); (c) ball milled at room temperature with aerosol spraying for 6h (MCA-6); (d) ball milled at about 95°C with aerosol spraying for 12h (MCA-12A); (e) ball milled at room temperature with aerosol spraying for 12h (MCA-12B), and (f) ball milled at about 95°C without aerosol spraying for 12h (MC-12).

Figure 3. The weight percentage of MgH₂ in the MgH₂ + 5 vol.% C mixture ball milled with aerosol spraying as a function of the aerosol spraying time. Note the linear decrease in the quantity of MgH₂ for 3h, 6h and 12 h ball milled samples under water cooling (MCA-3, MCA-6 and MCA-12B) are mainly due to the linear addition of LiBH₄ from aerosol spraying. However, the quantity of MgH₂ decreases significantly for 12h ball milled sample without water cooling (MCA-12A), indicating that there is additional mechanism(s) that leads to accelerated decrease in the quantity of MgH₂ during ball milling for MCA-12A.

Figure 4. X-ray diffraction pattern of the MgH₂ + 5 vol.% C mixture ball milled at about 95°C with aerosol spraying for 12 h: (a) XRD pattern ranging from 39° to 45° compared with the standard MgB₂ (04-014-0070) pattern, MgO (01-075-9568) pattern and MgH₂ (04-013-2314), and (b) its curve fitting via de-convolution; (c) XRD pattern ranging from 58° to 64° compared with the standard MgB₂ (04-014-0070) pattern, MgO (01-075-9568) pattern and MgH₂ (04-013-2314), and (d) its curve fitting via de-convolution.

Figure 5. X-ray diffraction patterns of the MgH₂ + 5 vol.% C mixture ball milled at 25°C with aerosol spraying: (a) for 3 h and (c) for 6 h with their XRD patterns ranging from 39° to 45° compared with the standard MgB₂ (04-014-0070) pattern, MgO (01-075-9568) pattern and MgH₂ (04-013-2314), and (b) and (d) the curve fitting of (a) and (c) patterns, respectively, via de-convolution.

Figure 6. X-ray diffraction pattern of the MgH₂ + 5 vol.% C mixture ball milled at 25°C with aerosol spraying for 12 h: (a) XRD pattern ranging from 39° to 45° compared with the standard MgB₂ (04-014-0070) pattern, MgO (01-075-9568) pattern and MgH₂ (04-013-2314) and (b) its curve fitting via de-convolution.

Figure 7. FTIR spectra of (a) the BMAS-processed sample with ball milling for 3 h (MCA-3), (b) the BMAS-processed sample with ball milling for 6 h (MCA-6), (c) the BMAS-processed sample with ball milling for 12 h (MCA-12A), (d) the starting material (the commercial MgH₂ powder plus carbon), and (e) the commercial KBr powder.

Figure 8. FTIR spectra ranging from 1800 to 2800 cm^{-1} : (a) the BMAS-processed sample with ball milling for 3 h (MCA-3), (b) the BMAS-processed sample with ball milling for 6 h (MCA-6), (c) the BMAS-processed sample with ball milling for 12 h (MCA-12A), (d) the starting material (the commercial MgH_2 powder plus carbon), and (e) the commercial KBr powder.