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Nanostructure-induced hydrogenation of layered compound MgB_2

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ABSTRACT

We investigated the hydrogenation properties of layered compound MgB_2 mechanically milled under a hydrogen pressure of 1.0 MPa. The total hydrogen concentration after milling for 600 min was approximately 1.0 mass%. No hydrogen insertion into MgB_2 interlayer was observed from interlayer distance analysis. On the other hand, mechanical milling generated the nanostructured MgB_2 with grain boundary defects in which B–H covalent bond and/or Mg–H bond were assumed to be formed. The nanostructure with grain boundary defects significantly promoted the subsequent high pressure (40.0 MPa) hydrogenation of MgB_2 for the synthesis of $Mg(BH_4)_2$ comprising $[BH_4]^-$ anions with B–H covalent bonds.

1. Introduction

Layered materials such as graphite [1] and hexagonal boron nitride (h-BN) [2], have been studied by mechanical milling under hydrogen atmosphere [3–7]. Generally, graphite and h-BN do not react with hydrogen, i.e. they cannot be hydrogenated; while the nanostructures formed by milling under hydrogen atmosphere led to the progress of hydrogenation [3,4,6]. In hydrogenated graphite, two types of hydrogen coordination have been observed, i.e. insertion of hydrogen into the graphite interlayer and formation of C–H covalent bonds in the grain boundary defects [3–5].

Similar to graphite, MgB_2 – a famous superconducting material [8] – is known to show a layered structure comprising boron honeycomb layers sandwiched between triangular Mg layers [9,10]. Such similarities arouse our interests in the material and motivate us to investigate whether mechanical milling of MgB_2 under hydrogen atmosphere initiates hydrogenation, which does not occur at room temperature and normal pressure.

Recently, MgB_2 has been reported to react with hydrogen to yield $Mg(BH_4)_2$ at 673 K under a high hydrogen pressure of 95 MPa for approximately 5 days according to reaction (1) [11].

$$MgB_2 + 4H_2 \rightarrow Mg(BH_4)_2 \quad (1)$$

$Mg(BH_4)_2$, having low temperature (hexagonal) and high temperature (orthorhombic) crystal structures, is a metal borohydride with high hydrogen density of 14.9 mass% [12–16]; metal borohydrides have the general formula $M(BH_4)_n$ (n indicates the valence of metal M), and in these compounds, hydrogen bonds covalently with boron to form the complex anion $[BH_4]^-$ [17]. In the layer structure of MgB_2, every boron atom mainly forms covalent bonds with three neighbor boron atoms [10]. These large differences in crystal structures [9,14] and bonding characteristics [10,17] between $Mg(BH_4)_2$ and MgB_2 suggest that the progress of reaction (1) would accompany the diffusion (migration) of Mg, B and H atoms. It is though that nanostructure with grain boundary defects would have the ability to promote the above mentioned atomic diffusion (migration) [18]. To our opinion, the detail promoting effect of nanostructures on the formation of $Mg(BH_4)_2$ from MgB_2 is needed to be studied.

In this study, the layered compound MgB_2 was mechanically milled under hydrogen atmosphere at room temperature. The objectives of the study were as follows: (i) to elucidate the relationship between the structural (including interlayer) changes and hydrogenation properties for different durations of the milling process and (ii) to experimentally investigate the promoting effect of nanostructures on the synthesis of $Mg(BH_4)_2$ according to reaction

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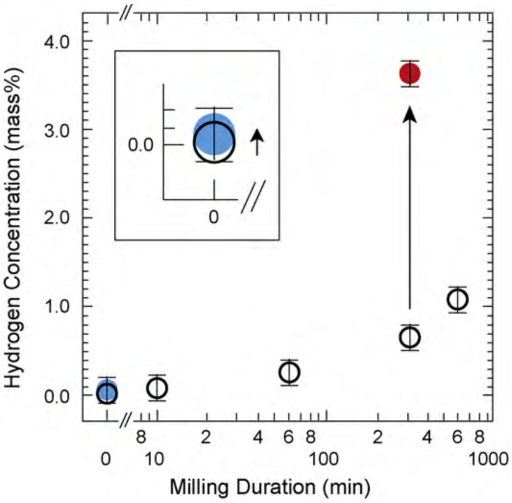

Fig. 1. Hydrogen concentrations (open circles) in MgB_2 mechanically milled under a hydrogen pressure of 1.0 MPa as a function of milling duration. The sample milled for 0 min indicates the host material. Hydrogen concentrations in MgB_2 subjected to high pressure hydrogenation treatment without being milled (blue close circle) and with 300 min milling (red close circle) are also shown for comparison. Inset presents the enlarged illustration of the values for MgB_2 samples milled for 0 min and that subjected to high pressure hydrogenation treatment. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

(1) by high pressure (40.0 MPa) hydrogenation.

2. Experimental

Commercially obtained MgB_2 (≥96% purity, −325 mesh, Aldrich) was used as the host material without pretreatment. No diffraction peaks of MgO were detected in the host MgB_2 although a thin oxide layer might cover the particle surface. Impurity of approximately 5 mass% of Mg was found in the host MgB_2 by Rietveld analysis using the RIETAN-2000. The host material was subjected to mechanical milling (Fritsch P-7) in a hardened steel vial with a ball to powder ratio of 20. The host material was milled under an initial hydrogen pressure of 1.0 MPa at room temperature for different durations ranging from 0 to 600 min. High pressure hydrogenation of selected samples was carried out in a powder state under a hydrogen pressure of 40.0 MPa at 673 K for 24 h in a specially designed pressure-resistant reaction tube. Changes in the crystal structure were determined by X-ray diffraction (XRD) measurement (PANalytical X'PERT with Cu Kα radiation). Hydrogen concentrations referred to the materials were determined by thermogravimetry (Rigaku TG-8210) through heating the samples up to 873 K at a rate of 5 K/min under a helium flow (150 ml/min). The constituents of selected samples after high pressure hydrogenation treatments were detected by ^{11}B magic angle spinning nuclear magnetic resonance (MAS NMR). ^{11}B MAS NMR measurements were carried out on JNM-ECA600 (JEOL Ltd.) spectrometer operating at magnetic field of 14.1 T. The resonance frequency of ^{11}B was 192.57 MHz and the spinning rate of the 4.0 mmϕ sample rotor was 16 kHz. Chemical shift was referenced to $BF_3(Et_2O)$ in ether solution as 0 ppm.

3. Results and discussion

Fig. 1 shows the hydrogen concentration in MgB_2 mechanically milled under a hydrogen pressure of 1.0 MPa. The hydrogen concentration gradually increases with the milling duration. The total hydrogen concentration after milling for 600 min is approximately 1.0 mass%. These results indicate that milling process gradually promoted the hydrogenation of MgB_2, similar to the case of graphite and h-BN [3–6].

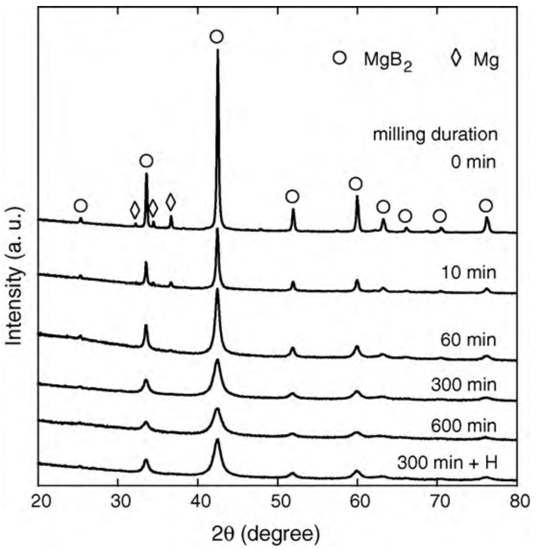

Fig. 2. Powder XRD profiles of MgB_2 milled for different durations at room temperature. The sample milled for 0 min indicates the host material. MgB_2 milled for 300 min followed by high pressure hydrogenation treatment is denoted as "300 min + H".

Changes in the structures of MgB_2 mechanically milled for different durations were determined by powder XRD measurement, and the results are presented in Fig. 2. No new phases were observed. To elucidate the relationship between the hydrogen concentration and the changes in the structure of the samples, the d-spacing of the (1 0 0) and (1 0 1) planes and the crystallite size were determined from the XRD profiles (Fig. 2) and the values were plotted as a function of the milling duration (Fig. 3). Both d-spacings did not change noticeably with an increase in the milling duration, which suggest that hydrogen was not inserted into the MgB_2 interlayer. On the other hand, the crystallite size, which was estimated using the Williamson–Hall equation [19], drastically decreased to approximately 18 nm when the milling duration exceeded 300 min. This significantly decreased crystallite size suggests an increase in the volume fraction of grain boundary defects [18]. Therefore, hydrogen in the nanostructured MgB_2 was thought to form B–H bonds and/or Mg–H bonds in grain boundary defects. Although the exact H-related bonding characteristic in the nanostructured MgB_2 is needed to be clarified, the possibly formed B–H covalent bonds are considered to be similar to the C–H covalent bonds formed in nanostructured graphite [3–5]. B–H covalent bonds have also been detected in a defective structure of amorphous B [20].

Nanostructures with grain boundary defects significantly promoted the subsequent high pressure hydrogenation of MgB_2 for the synthesis of $Mg(BH_4)_2$ composed of $[BH_4]^-$ anion with B–H covalent bond. The hydrogen concentrations in MgB_2 that were subjected to high pressure hydrogenation without being milled

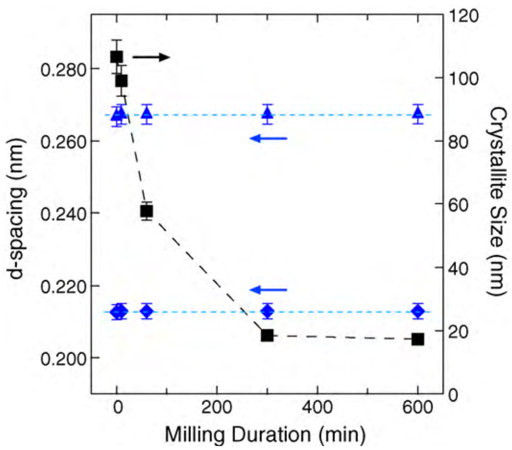

Fig. 3. d-Spacings corresponding to (1 0 0) (blue close triangles) and (1 0 1) (blue close rhombuses) planes and crystallite sizes (close squares) of MgB_2 milled for different durations at room temperature. The sample milled for 0 min indicates the host material. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

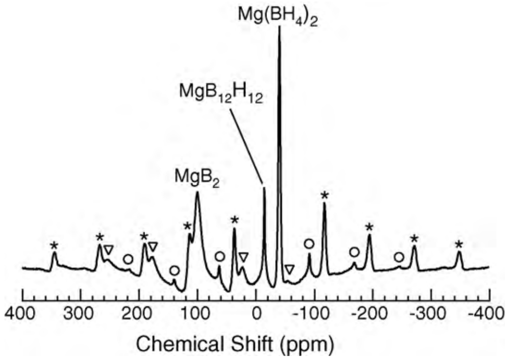

Fig. 4. ^{11}B MAS NMR measurement result of MgB_2 milled for 300 min and subjected to high pressure hydrogenation treatment. Inverted triangles, circles and asterisks denote the spinning sidebands of MgB_2, $MgB_{12}H_{12}$ and $Mg(BH_4)_2$, respectively.

and samples that were milled for 300 min and subjected to high pressure hydrogenation treatment are shown in Fig. 1. In the former sample, the hydrogen concentration was nearly 0 mass%, that is, hydrogen hardly reacted with MgB_2 during the high pressure hydrogenation treatment. In contrast, in the latter sample, the total hydrogen concentration reached a value as high as 3.6 mass%. The constituents of the latter sample were then identified by ^{11}B MAS NMR measurements and the results are presented in Fig. 4. A centerband peak that can be attributed to MgB_2 was clearly observed at 100.5 ppm [21]. In addition, peaks corresponding to $MgB_{12}H_{12}$ and $Mg(BH_4)_2$ were also detected at -14.1 and -40.0 ppm [16], respectively. It should be emphasized that $Mg(BH_4)_2$ was synthesized by high pressure hydrogenation of nanostructured MgB_2. This shows a good agreement with the recent report [11], i.e. the progress of reaction (1) was confirmed in both cases. The yields of $Mg(BH_4)_2$ from MgB_2, defined as the hydrogen concentration ratio between the hydrogenated MgB_2 and $Mg(BH_4)_2$, for the recent report [11] and the present study, are calculated as 75% and 24%, respectively. It is considered that the progress of reaction (1) would accompany the diffusion (migration) of Mg, B and H atoms. Therefore, the formation of $Mg(BH_4)_2$ would be kinetically affected by the nanostructures with grain boundary defects prepared by mechanical milling of MgB_2, as well as the high pressure hydrogenation conditions including temperature, pressure and duration. In other words, the different milling processes and high pressure hydrogenation conditions resulted in the different yield of $Mg(BH_4)_2$.

From the unchanged diffraction peaks of MgB_2 before and after high pressure hydrogenation (Fig. 2), the product $Mg(BH_4)_2$ is thought to be formed in grain boundary defects. That is, hydrogenation reaction of MgB_2 only occurred in grain boundary defects in both milling and the subsequent high pressure hydrogenation processes under the present experimental conditions. Nanostructures with grain boundary defects are expected to possess the advantages to offer abundant nucleation sites for $Mg(BH_4)_2$ and to provide fast diffusion (migration) paths [21] for Mg, B and H atoms, thus promote the formation of $Mg(BH_4)_2$.

Although providing a definitive description of hydrogenation mechanism is currently not possible, the nanostructures with grain boundary defects formed by milling may be a key factor responsible for the promotion of hydrogenation in MgB_2. An optimized mechanical milling process would highly moderate the hydrogenation condition of MgB_2 for the synthesis of $Mg(BH_4)_2$.

4. Conclusions

In summary, nanostructured MgB_2 with grain boundary defects was obtained by mechanical milling under a hydrogen pressure of 1.0 MPa at room temperature. The hydrogen concentration in MgB_2 increased with the milling duration. The total hydrogen concentration after milling for 600 min was approximately 1.0 mass%. The absence of any change in the interlayer distance for different milling durations suggested that no hydrogen was inserted into the MgB_2 interlayer. The significantly decreased crystallite size suggests an increase in the volume fraction of grain boundary defects with the milling duration. Hydrogen was assumed to form B–H covalent bonds and/or Mg–H bonds in the grain boundary defects of nanostructured MgB_2. Furthermore, nanostructures with grain boundary defects significantly promoted the subsequent high pressure hydrogenation that led to the formation of $Mg(BH_4)_2$. It was suggested that the nanostructures with grain boundary defects may be a key factor responsible for the promotion of hydrogenation in MgB_2. These findings suggest a viable approach for preparing various $M(BH_4)_n$ comprising the complex anion $[BH_4]^-$ with B–H covalent bonds.

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