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DSC study of the effect of milling conditions on the hydrogen storage properties of boron

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Abstract Two milling modes (shearing and impact) were applied to investigate the hydrogen storage properties of boron. It was found that the shearing mode leads to 2.05 wt% hydrogen trapped in boron, while impact mode to 2.93 wt%. Differential scanning calorimetry (DSC) was used to study thermally induced transformations in freshly milled and aged samples. The DSC traces obtained from freshly milled samples through the shearing and impact modes are dissimilar and are also very different from those obtained from the aged samples. The origins of these differences are discussed in relation to the milling mode applied.

Introduction

Intensive research on synthesizing and tailoring materials with high hydrogen storage capability and long cycle life has been carried out worldwide. Currently, elements with small atomic number such as lithium and boron are attracting tremendous attention because they are essential elements in some very promising hydrogen storage materials such as $LiAlH_4$ and $LiBH_4$ [1, 2]. One of boron hydrides, $NaBH_4$, has already been commercialized by Millennium Cell as part of the Hydrogen on Demand^{TM} process. Apart from hydrides, nanostructral forms of boron nitride such as nanocapsules, nanotubes, nanocages, nanoparticles, and nanoclusters have also been studied recently and are expected to appear in prospective applications [3, 4]. There are not many reports about boron itself being used to store hydrogen. Wang [5, 6] found 2.3 wt% hydrogen trapped in ball-milled amorphous boron. There are three types of B–H interaction, i.e. physisorbed H_2, B–H terminal bonds and B–H–B bridge bonds. The bridge bonds constituted a smaller percentage and decomposed at lower temperature compared to the terminal bonds.

It is well known that the defect formation and chemical reactions occurring during ball milling are dependent on many factors, such as milling mode, milling time, milling atmosphere, weight ratio of ball to powder, and so on. Different products have been obtained through different ball milling modes, although the starting materials, milling atmosphere, milling time, etc. were the same [7].

Since B–H terminal bonds and B–H–B bridge bonds make different contributions to the release of hydrogen trapped during ball milling, the properties of the as-milled samples can be adjusted via modifying these two bonds. In this work, we used two ball milling modes, low-energy shearing mode and high-energy impact mode, with the aim of studying their effects on

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hydrogen absorption. In this paper, relevant results are presented.

Experimental

Boron powder with a purity of 99.95% was milled under hydrogen in a magneto-mill, Uni-Ball-Mill 5 [8] under elemental milling modes such as impact and shearing (Fig. 1). The milling cylinder was evacuated and purged several times using helium firstly and then filled up with hydrogen gas up to 500 kPa pressure. The milling time was 100 h. For comparison, boron powder was milled in helium atmosphere using the same milling conditions.

In the shearing mode (Fig. 1a), the balls both rotate and oscillate around an equilibrium position at the bottom of the milling cylinder in a strong magnetic field. In the impact mode, the ball movement during the milling process is confined to the vertical plane by the cylinder walls and is controlled by an external magnetic field (Fig. 1b). In both cases, the magnetic field is generated by FeNdB magnets. The intensity and direction of the magnetic field can be externally adjusted, allowing the ball trajectories and impact energy to be varied in a controlled manner [7]. The sample ball milled in hydrogen using shearing mode was designated as SH and the one using impact mode as IH. In the same way, the sample ball-milled in helium through shearing mode was designated as SHe, through impact mode as IHe.

Differential scanning calorimetry (Perkin-Elmer DSC-4) was performed on the samples, with an argon flow rate of 70 ml/min at a heating rate of 20 °C/min up to 500 °C. To determine the hydrogen content absorbed during ball milling, carbon–hydrogen–nitrogen (CHN) analysis was carried out using a Carlo Erba Elemental Analyser Model 1106.

Results and discussion

DSC traces of fresh SH samples are shown in Fig. 2. Apart from three major endothermic peaks situated at 105 °C, 150 °C, and 170 °C, respectively, many small endothermic peaks were observed in the range of 190–350 °C. A descending trend at higher temperature was observed and the possible origin will be discussed later. In the case of IH, two big endothermic peaks are visible, with one at 147 °C and the other at 402 °C (Fig. 3). As a contrast to the SH sample, there are several exothermic-like effects occurring between these two large endothermic peaks. Major endothermic peaks are not visible in the second run curve, which implies that during the first run, hydrogen was released as indicated by CHN analysis. Also, all the small peaks disappeared and this will be discussed later.

The combustion analysis shows that 2.05 wt% hydrogen was trapped in the as-milled SH, while 2.93 wt% hydrogen was trapped in the as-milled IH. This indicates that impact mode contributes more to the hydrogen absorption than shearing mode. However, after heating the as-milled sample to 500 °C and holding at this temperature for 5 min, 1.24 wt% hydrogen still existed in the SH, and only 0.5 wt% was left in the IH. These data imply that the ratio of strong B–H bonds in SH to the weak bond types is much higher than in the IH.

The different types of DSC behaviour, the amount of trapped hydrogen during milling, and the amount of residual hydrogen after heating are presumably related to the milling mode, more specifically, to the move-

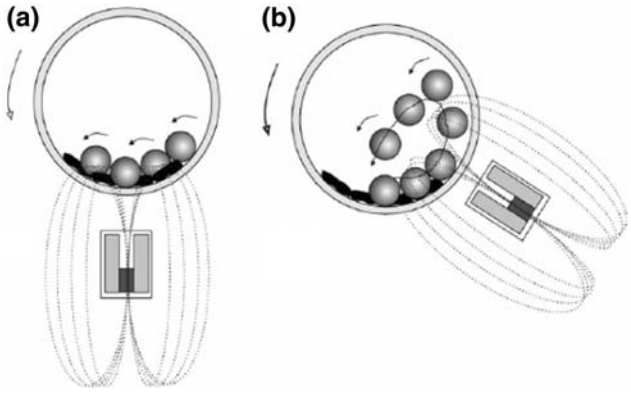

Fig. 1 The Uni-Ball-Mill 5 with the FeNdB external magnets operating in the shearing (**a**) and the impact (**b**) modes of milling [7]

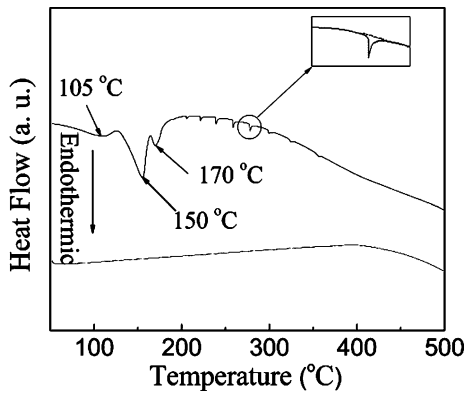

Fig. 2 DSC traces of the fresh SH

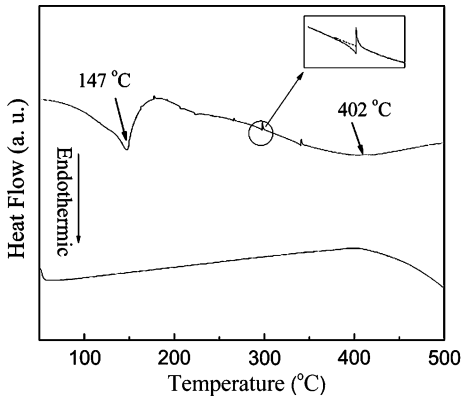

Fig. 3 DSC traces of the fresh IH

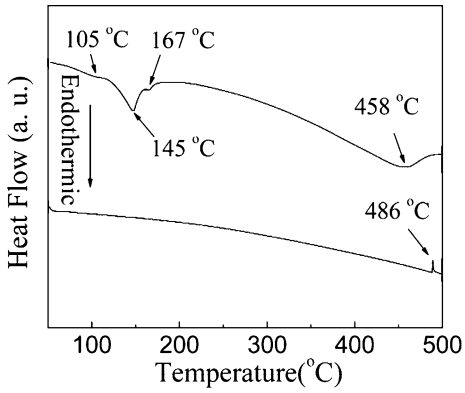

Fig. 4 DSC traces of the aged SH

ment of balls in the cylinders and the energy applied during ball milling. Impact mode is a high-energy type of ball milling, and the balls continuously collide with the wall of the cylinder, resulting in a high local temperature. In addition, impact generates more structural defects, which improves the diffusion rate (together with temperature) and improves capacity. In contrast, shearing mode is a low-energy type of milling, and the balls roll along the wall, which acts to grind the powders in the cylinder. This mode does not favour the formation of structural defects to such a degree as impact mode. Moreover, the local temperature is unable to rise as high as in the case of impact mode, which may also affect the reaction between boron and hydrogen.

Wang et al. [5] found that the amount of hydrogen trapped by bridge bonds was approximately half as great as that trapped by terminal bonds, and they were desorbed at 200 °C and 450 °C, respectively. In their work, ball milling was carried out through a planetary ball mill apparatus (Fritsch 7) at 400 rpm, in which the movement of balls is quite chaotic, with shearing and impact occurring irregularly, but with impact predominant. In this work, the effects attributed to shearing were separated from those of impact by using these two milling modes. We believe that the endothermic effect occurring at 140 °C is due to the breaking of B–H–B bridge bonds, and the other at 402 °C (for IH) is attributed to the breaking of B–H terminal bonds. For SH, the descending trend in Fig. 2 is presumably associated with the breaking of B–H terminal bonds, which is postponed to a higher temperature. Apart from this difference, a very notable DSC observation is the series of endothermic effects for SH in contrast to the exothermic-like effects for IH. Possible origins will be discussed later in the paper.

Figure 4 and Fig. 5 present the DSC traces of the SH and IH after 2 weeks aging. These traces are quite different from those of the freshly milled samples, which indicates that the milled samples experienced structural change during the aging. In the case of SH (Fig. 4), all the small endothermic effects have vanished and a broad endothermic peak at 458 °C has appeared. In the case of IH (Fig. 5), the endothermic peak at 147 °C in the fresh sample (Fig. 3) has split into three endothermic peaks, which are similar to those of aged SH. The broad peak at 402 °C obtained from the fresh sample was shifted to 485 °C. Another remarkable difference is that all the small exothermic-like peaks have disappeared. All the endothermic peaks associated with hydrogen desorption disappeared in the second run curves for both samples.

Figure 6 and Fig. 7 show DSC traces obtained from the as-milled boron in helium. The purpose of this experiment was to investigate thermal effects due to recrystallization of ball-milled boron and distinguish these effects from effects due to B–H interaction. Since the reaction between boron and iron from the steel

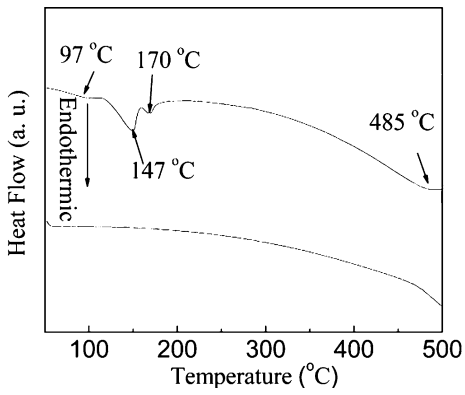

Fig. 5 DSC traces of the aged IH

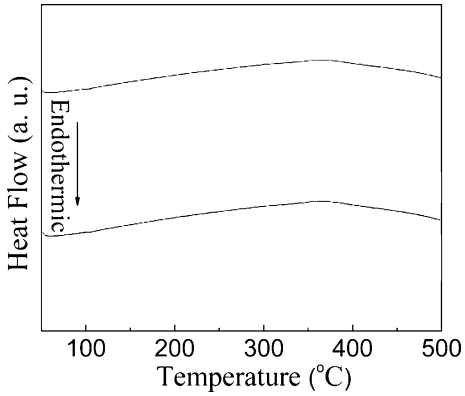

Fig. 6 DSC traces of the fresh SHe

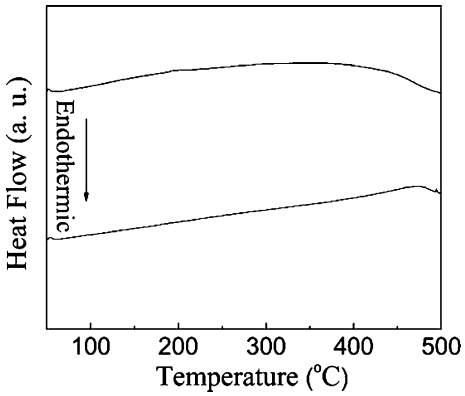

Fig. 7 DSC traces of the fresh IHe

materials is negligible, all the thermal effects are considered to be associated with the structural evolution of boron upon heating. There is no clear heat absorption or desorption in the case of the SHe sample. The second run curve of SHe is very similar to that of the first run, which means that the first run heat treatment did not alter the properties of the as-milled sample. There is an exothermic peak at around 475 °C for the IHe sample in the second run curve, which at this stage is difficult to explain. However, the DSC curves do show the different milling effects associated with the different mill modes. Taking into account the different milling atmospheres, the series of endothermic and exothermic-like peaks obtained from fresh SH (Fig. 2) and IH (Fig. 3) are due to the interaction between boron and hydrogen, since all the other milling conditions remained the same. It is well known that boron is the only element other than carbon that can build molecules of unlimited size (boron clusters) by covalently bonding, and boron can form various forms of polyhedral borane [9]. From our own experiments we found that graphite forms a variety of hydrogenated carbon clusters during ball milling in hydrogen [10], and the DSC curves of the ball milled graphite also display similar small peaks. Results are submitted for publication. The small peaks are believed to be associated with the hydrogen desorption from hydrogenated carbon clusters and subsequent rearrangement of carbon atoms [11].

As can be seen in the inset (Fig. 3), the small exothermic-like peak actually is an endothermic peak followed by an exothermic peak, which is presumably due to the hydrogen desorption from the hydrogenated boron cluster (endothermic effect) and subsequent boron atom re-arrangement, resulting in rapid formation of larger boron clusters (exothermic effect). As can be deduced from the different positions of the small peaks, the desorption temperatures are determined by the distinct hydrogenated boron clusters. On the contrary, the small endothermic peak enlarged in Fig. 2 shows an endothermic effect only. It is very likely that in this case B–H molecules decompose but there is no following formation of boron clusters. The difference probably originates from the milling mode. The high-energy impact mode leads to the formation of highly disordered atomic arrangements, which results in evident exothermic effects due to the microstructural evolution during heating. In contrast, the low energy shearing mode results in fewer defects and no apparent atomic re-arrangement during heating. It seems that the small hydrogenated boron clusters are not chemically stable, and after 2 weeks the small DSC peaks disappeared (Fig. 4 and Fig. 5).

Conclusion

On the basis of the above results one can conclude that different ball-milling modes lead to dissimilar amounts of hydrogen trapped by boron. Additionally, the interaction between boron and hydrogen depends on the milling mode applied, with the low-energy mode resulting in a higher percentage of strong B–H bonds, in contrast to the higher percentage of weak B–H bonds in boron milled at high-energy.

In the case of the samples obtained from shearing mode, there are many small endothermic peaks coexisting with bigger endothermic ones, which correspond to hydrogen desorption. Many small exothermic-like peaks, however, are visible for the sample obtained through impact. For both cases, all these small peaks disappear after 2 weeks aging.

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