Fig. 4. XRD patterns of the synthesized nanocomposite (Mn(BH$_4$)$_2$ + 2LiCl) after dehydrogenation at 100 °C for 18.7 h.

Fig. 5. (a and c) TEM micrograph of the synthesized nanocomposite (Mn(BH$_4$)$_2$ + 2LiCl) (dry condition) after dehydrogenation at 100 °C (18.7 h) and (b and d) corresponding selected area electron diffraction (SAED) patterns.

\[
\text{Mn(BH$_4$)$_2$ + 2LiCl} \rightarrow \frac{1}{3}\text{Mn} + \frac{4}{3}\text{B} + \frac{1}{3}\text{B}_2\text{H}_6 + 3\text{H}_2 + [2\text{LiCl}]
\]

(3)

The theoretical capacity of reaction (3) is 3.58 wt.% H$_2$ and 9.0 wt.% for a gas mixture ($3\text{H}_2 + \frac{1}{3}\text{B}_2\text{H}_6$). In reactions (2) and (3) both Mn and B are being formed so the microstructural phase composition of samples after reactions (2) and (3) is the same.

The XRD pattern for the synthesized nanocomposite (Mn(BH$_4$)$_2$ + 2LiCl) after dehydrogenation at 100 °C for 18.7 h is presented in Fig. 4 and after dehydrogenation at 150 and 200 °C.
Table 2
Interplane spacings and Bragg diffraction angles 2θ for α-Mn as compared to experimentally observed TEM SAED patterns.

<table>
<thead>
<tr>
<th>α-Mn ICDD (JCPDS) card #32-0637</th>
<th>(SAED) this work</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_{006} (Å)</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>d_{006} (Å)</td>
</tr>
<tr>
<td>210.110</td>
<td>1.06</td>
</tr>
<tr>
<td>182.990</td>
<td>2.50</td>
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<tr>
<td>181.900</td>
<td>9.0</td>
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<tr>
<td>174.750</td>
<td>1.40</td>
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<tr>
<td>128.940</td>
<td>4.0</td>
</tr>
<tr>
<td>126.050</td>
<td>7.0</td>
</tr>
</tbody>
</table>

respectively. The most intense diffraction planes for α-Mn are collected in Table 2 including the lattice spacings (d_{006}) and peak intensities. According to Table 2 the strongest peak (100%) of α-Mn is assigned to the (330) plane with the d_{330} spacing of 2.10 Å. The SAED patterns of annealed powder in Fig. 5b and d show strong diffraction spots of α-Mn corresponding to the diffraction planes (330), (510) and (550) (Table 2) distributed on the calculated diffraction rings which were calculated by the ImageJ software [20] based on the scale of the corresponding SAED pattern.

The first three strongest diffraction peaks of β-B occur at small diffraction angles of 2θ = 11.12°, 17.51° and 19.02° and conversely at larger d_{006} spacings whose corresponding electron diffraction spots would be located very close to the center of SAEDs in Fig. 5b and d. Unfortunately, they cannot be discerned in the respective SAED patterns because of the presence of a background coming from the fact that the particles are very small and distributed over an amorphous carbon film in Fig. 5b and d. Nevertheless, two electron diffraction spots from the lattice planes (205) and (401) with the lattice spacing d_{002} = 2.34 Å and d_{205} = 3.31 Å, belonging to β-B, are clearly detected in the SAED patterns in Fig. 5b and d.

The evidence that both Mn and B exist in the dehydrogenated powder as the crystalline phases α-Mn and β-B, respectively, is another important finding in this work. It was shown earlier that the XRD pattern of the dehydrogenated (Mn(BH₄)₂ + 2LiCl) nanocomposite shown in Fig. 4 does not show any visible Bragg diffraction peaks belonging to crystalline Mn or B. In the cases where no crystalline diffraction peaks are present it is often assumed “a priori” that the decomposition products of Mn(BH₄)₂ are amorphous [11,12,15]. However, to the contrary, the SAED patterns clearly show that both Mn and B products exist after dehydrogenation of Mn(BH₄)₂ in a crystalline form. For the sake of clarity, it is to be noted that in [16] we observed very small but recognizable diffraction peaks of α-Mn after dehydrogenation of the synthesized mixtures (nLiBH₄ + MnCl₂) where n = 5, 9 and 23. No XRD peaks corresponding to crystalline α-Mn have ever been observed for

![Fig. 6](image-url)  
(a) The energy X-ray dispersive spectroscopy (EDS) elemental distribution map after dehydrogenation at 100 °C (18.7 h) and decomposition of Mn(BH₄)₂ for all elements: C (red), Mn (green) and B (blue). Individual elemental distribution maps for (a) C, (c) Mn and (d) B. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
the molar ratio \( n = 2 \). Neither XRD peaks of crystalline \( \beta \)-B have ever been observed after dehydrogenation of \( \text{Mn(BH}_4\text{)}_2 \) for any molar ratio \( n \) in the \((\text{LiBH}_4 + \text{MnCl}_2)\) mixture \([2,3,6-12,15]\).

In general, it must be pointed out that from reactions (2) and (3) the quantity of LiCl after deconcentration is 2 mol in the total mass of powder which is much larger than only 1 mol of Mn or B. Therefore, LiCl will be well detectable by XRD in contrast to Mn/B whose quantity could be insufficient to be detectable by XRD although Mn/B are detectable by electron diffraction which is capable of analyzing very small powder particles. The SAEDPs in Fig. 5a and c were taken from powder particles (red arrows) having sizes on the order of 20–50 nm. Since the SAEDPs show diffraction spots of LiCl, \( \alpha \)-Mn and \( \beta \)-B, all these phases must have nanometric sizes to be confined within the 20–50 nm sized particles. Additional support for the presence of nanometric-size \( \alpha \)-Mn and \( \beta \)-B after thermal dehydrogenation of the \((\text{Mn(BH}_4\text{)}_2 + \text{MnCl}_2)\) nanocomposite and decomposition of \( \text{Mn(BH}_4\text{)}_2 \) is provided by the EDS elemental distribution map for all elements: Cl (red), Mn (green) and B (blue) in Fig. 6a and particularly by the individual elemental maps for Cl (Fig. 6b), Mn (Fig. 6c) and B (Fig. 6d) from the powder thermally dehydrogenated at 100 °C for 18.7 h whose XRD pattern is already shown in Fig. 4 and HR TEM images and SAED patterns are shown in Fig. 5. For comparison to Fig. 6 the same EDS elemental distribution maps were taken from a synthesized nanocomposite \((\text{Mn(BH}_4\text{)}_2 + \text{MnCl}_2)\) after ball milling and are shown in Fig. 7. It is clearly seen, especially from individual EDS elemental maps that both the \( \text{MnK} \alpha_1 \) (Fig. 7c) and \( \text{BK} \alpha_2 \) (Fig. 7d) elements are very uniformly dispersed in the ball-milled powder containing the synthesized Mn(BH)_4 phase while after thermal decomposition of Mn(BH)_4 the Mn element, as can be seen in its MnK \alpha_1 \) elemental map (Fig. 6c), is agglomerated into clusters, most likely, forming the \( \alpha \)-Mn nanograins. There is no such a pronounced clustering observed in the elemental BK \alpha_2 \) map (Fig. 6d) for dispersion of \( \beta \)-B after decomposition of Mn(BH)_4, as compared to its dispersion after ball milling in the elemental BK \alpha_2 \) map in Fig. 7d.
A high resolution TEM image of the synthesized nanocomposite after thermal dehydrogenation (Figs. 4 and 5) is shown in Fig. 8a which was taken from one of the powder particles visible in Fig. 5c. Nanograins with different crystal orientations, which are contoured by a red broken line, can be clearly seen. Employing FFT from the rectangle area indicated in Fig. 8a identifies these nanograins as belonging to LiCl. The digital diffraction patterns obtained using FFT in Fig. 8b presents two calculated electron diffraction rings which exactly conform to the diffraction pattern of the fcc structure of LiCl. The average ECD for the LiCl nanograins visible in Fig. 8a was estimated as being equal to 6.1 ± 1.8 nm. This value correlates well with the nanograin size of the LiCl phase after MCAS synthesis observed in the ball milled powder particles (Fig. 3).

4. Summary and conclusions

Mechano-chemical activation synthesis (MCAS) using a magnetic ball mill was employed to synthesize the nanocomposite (Mn(BH₄)₂ + 2LiCl) from the initial (2LiBH₄ + MnCl₂) powder mixture. Ball milling was carried out under the milling energy input Qₘₐₐ₃ = 145.6 kJ/g. Both X-ray diffraction and TEM selected area electron diffraction patterns (SAEPs) clearly confirm the presence of the Mn(BH₄)₂ and LiCl phases in the synthesized nanocomposite. No other phases were detected. Both Mn(BH₄)₂ and LiCl are nanocrystalline phases because bright field high-resolution TEM imaging of the synthesized composite powder reveals the presence of nanograins belonging to LiCl and Mn(BH₄)₂. The grain sizes expressed as the equivalent circle diameters (ECD) of LiCl and Mn(BH₄)₂ estimated from the high-resolution TEM micrographs, are within the range of 14.1 ± 3.7 nm and 10.0 ± 2.9 nm, respectively. The XRD patterns of the thermally dehydrogenated (Mn(BH₄)₂ + 2LiCl) do not exhibit any visible Bragg diffraction peaks belonging to either crystalline α-Mn or β-B. In contrast, the SAEP patterns and EDS elemental maps provide convincing evidence that both Mn and B exist in the dehydrogenated powder as the nanometric-size phases α-Mn and β-B, respectively. Apparently, the lack of Bragg diffraction peaks in an XRD pattern is insufficient evidence that the Mn and B elemental products of Mn(BH₄)₂ thermal dehydrogenation can be classified as being amorphous.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.actamat.2015.08.036.

References


4.7. Weight percent of a hydride phase and hydrogen by DSC method

In DSC measurements, the weight percent of a phase can be calculated using the peak area of the DSC curve and its reported heat of formation (enthalpy of formation) if it is available. For example, weight percent of the $\beta$-MgH$_2$ in a reactively milled powder can be estimated using the peak area of the DSC curves and the reported $\beta$-MgH$_2$ heat of formation (−74 kJ/mol [116], which equals to -2811 J/g). The DSC curve was analyzed by the NETZSCH thermal analysis software. First, the onset and end temperature of the peak were determined. Then, the peak area was calculated using the linear approach from the onset temperature to the end temperature (Fig. 4.14) by the DSC software.

The weight percent of $\beta$-MgH$_2$ is given by:

$$\text{wt\% of } \beta\text{-MgH}_2 = \frac{\text{peak area (J/g)}}{\beta\text{-MgH}_2 \text{ heat of decomposition (J/g)}}$$

where heat of decomposition = −(heat of formation)

From the decomposition of $\beta$-MgH$_2$ ($\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$), the weight percent of desorbed hydrogen can be calculated by:

$$\text{wt.\% of H}_2 = \text{wt.\% of MgH}_2 \times \left(\frac{\text{molecular weight of H}_2}{\text{molecular weight of MgH}_2}\right)$$

Fig. 4.14. Schematic of calculating the weight percent of a hydride phase by DSC analysis [10].

References


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