

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The hydrogen desorption/absorption properties of the modified LiBH_4 and MgH_2 mixture (mixture) including hydrogen desorption temperature, amount of desorbed hydrogen, and reversibility were investigated. In the first part, the hydrogen desorption/absorption behaviors and the mechanism of the mixture ball-milled for 1 h were reported. It was found that the mixture decomposed in three steps at 50, 380, and 450°C, respectively, in the first desorption. The total amount of desorbed hydrogen was 8.6 wt%. In the subsequent desorption, the mixture released hydrogen in two steps at 360°C. The total amount of released hydrogen was further reduced to 5.4 and 1.8 wt% in the second and the tenth desorption, respectively. For the decomposition mechanism, at a temperature lower than 350°C or the first step of the first desorption, the XRD patterns exhibited that LiBH_4 and MgH_2 partially decomposed to $\text{LiBH}_{4-x}/\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{MgH}_{2-y}/\text{Mg}$, respectively. At 400°C or the second step of the first desorption, it was found that the spent hydrides further decomposed to LiH and Mg . At 450°C or the third step of the first desorption, the formation of MgB_2 and LiH was from the spent hydrides. After the first hydrogen absorption, LiBH_4 and MgH_2 were recovered in the mixture. The unconverted phases of LiH , MgB_2 , and MgO could be the reason for the decrease in the reversible hydrogen desorption capacity. In addition, the presence of MgB_2 was the primary factor for the reversibility of the mixture. After that, 3 mol% of TiCl_3 , ZrCl_4 , and HfCl_4 were added to the mixture and ball-milled for 1 h. The results showed that the sample doped with TiCl_3 released hydrogen at the lowest desorption temperature (260°C).

The ball-milling time, the titanium catalysts, and the initial system pressure affected the hydrogen desorption/absorption properties of the mixture. For the ball-milling time, it was found that all the mixtures with the different ball-milling times of 1, 5, and 10 h started to release hydrogen at the same temperature of 50°C. The

mixture ball-milled for 5 h had the highest hydrogen desorption capacity of 9.2 wt% in the first desorption. For the subsequent desorption, the mixture ball-milled for 10 h released hydrogen at the lowest desorption temperature of 340°C. The sample also had the highest reversible hydrogen capacity in the range of 4.2-5.4 wt% in the second to the fourth desorption. The lower hydrogen desorption temperature and better reversibility of the mixture ball-milled for 10 h was a consequence of the lower crystallite size due to the prolonged milling time. Comparison of the total hydrogen desorption capacity released from the mixture ball-milled for 1, 5, and 10 h in the first and the fourth desorption is shown in Figure 8.1(a).

3 mol% of Ti, TiO₂, and TiCl₃ were added to the mixture and ball-milled for 5 h. The results in the first desorption of the mixtures showed that the undoped and doped mixtures started to desorb hydrogen at the same temperature of 50°C. The sample doped with TiCl₃ released hydrogen in one step, while the other mixtures decomposed in three steps. This indicated better catalytic activity of TiCl₃ than the other catalysts. In the subsequent desorption, all mixtures decomposed in two steps, the TiCl₃ doped sample started to release hydrogen at the lowest hydrogen desorption temperature. The Ti doped sample had the highest reversible hydrogen desorption capacity. A possible reason is due to Ti has a much lower chance to form any inactive by-products as it does not contain O²⁻ as in TiO₂ or Cl⁻ as in TiCl₃. The total amounts of desorbed hydrogen from the undoped and doped mixture are compared in Figure 8.1(b). In addition, the XRD patterns exhibited the effects of the titanium catalysts in the hydride crystallite size reduction.

The initial system pressure was found to affect the reversibility of the LiBH₄/MgH₂ mixture ball-milled for 5 h. The total amount of desorbed hydrogen from the first desorption was reduced from 9.0 wt% in the sample decomposing under 0.1 MPa hydrogen pressures to 6.5 wt% in the sample decomposing under 0.2 MPa hydrogen and argon pressures. The lower desorbed hydrogen amount was mainly influenced from the decomposition of LiBH₄. At the fourth desorption, the sample decomposing under 0.1 MPa hydrogen pressure was significantly reduced to 1.3 wt%, while the sample decomposing under 0.15 and 0.2 MPa hydrogen and argon pressures was reduced to 4.9, 4.6, and 4.1 wt%, respectively. The reversibility

of the system seems to increase with the initial system pressure. The total amounts of hydrogen in the first and the fourth desorption were shown in Figure 8.1(c). In addition, the increase in the initial system pressure also increases the decomposition temperature of the sample.

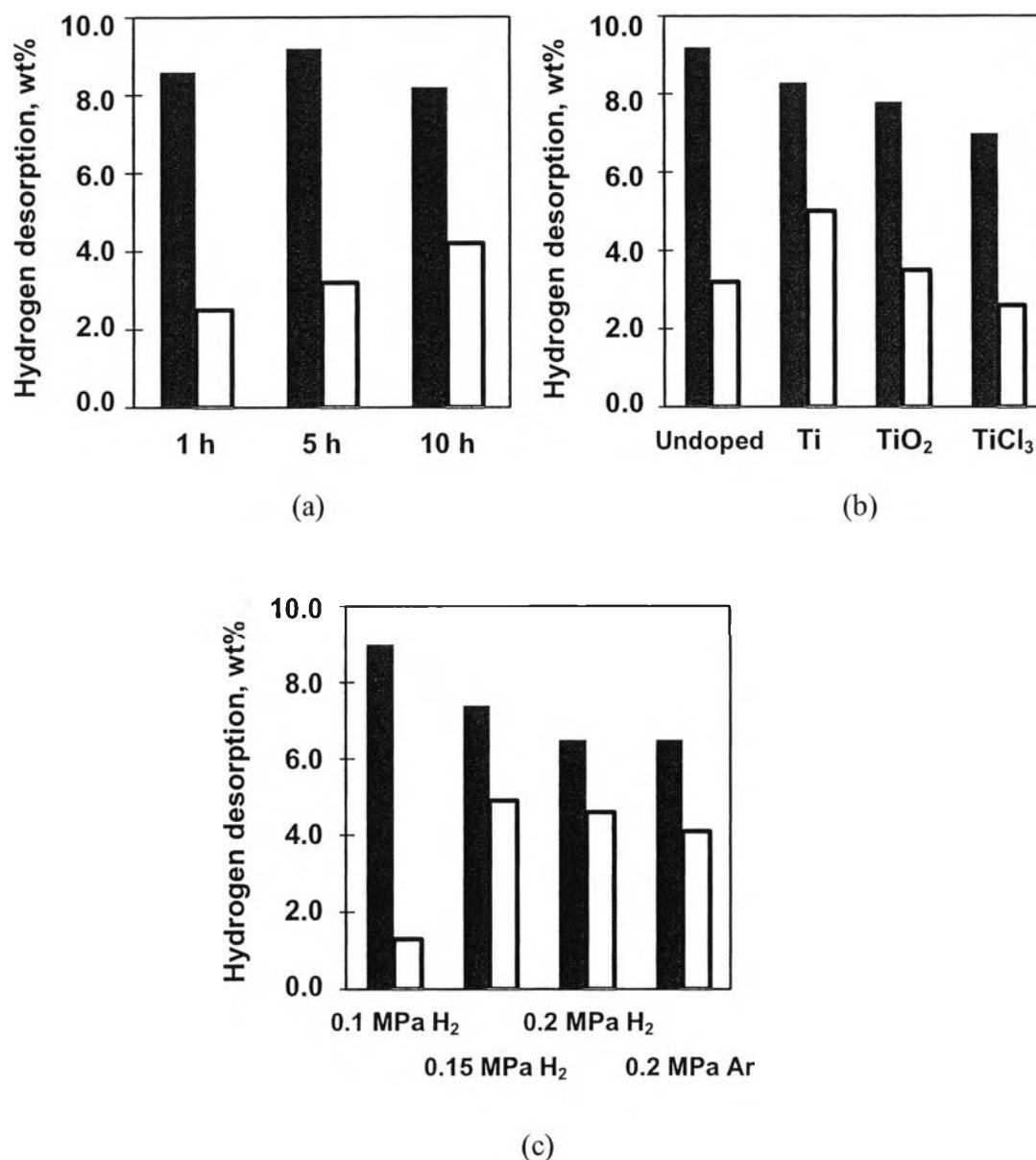


Figure 8.1 Comparison of the total amounts of desorbed hydrogen in the first and the fourth desorption of the LiBH₄/MgH₂ mixture (a) with different ball-milling times, (b) doped with the titanium catalysts, and (c) decomposing under different initial pressures.

8.2 Recommendations

Recommendations for further hydrogen storage research are:

- The system should be conducted in the dynamic vacuum pressure in order to avoid the effect of released pressure on the hydrogen desorption of the hydride.
- The hydrogen desorption temperature at lower than 285°C should be operated to prevent the melting of LiBH₄, which leads to the hydride accumulation.
- The ball-milling time up to 100 h should be conducted to see the hydrogen decomposition behaviors of the hydride.
- The other catalysts such as Nb and Ni compounds should be used.
- The other borohydride compounds, which have a lower hydrogen desorption temperature than LiBH₄ and a high hydrogen capacity, such as Mg(BH₄)₂ and Al(BH₄)₃ should be studied.
- The hydrogen storage in chemical hydrides such as ammonia borane and guanidinium borohydride, which have a high hydrogen capacity and a lower desorbed temperature than the metal hydrides, should be studied in details.

