

## **Mechanical Destabilization of Light Metal Hydrides**

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### **Introduction**

One of the major challenges for developing materials for hydrogen storage is to reduce the desorption temperature of light metal hydrides based on magnesium. This can be accomplished, to some extent, by alloying with elements that reduce the stability of the hydrides. Although there are many such studies reported in literature, none of the alloying elements have so far provided a substantial decrease in hydride stability without also significantly reducing hydrogen capacity. The present study represents an alternative approach to the problem. Instead of compositional modification of magnesium-based alloys, the hydrides are partially destabilized by mechanical treatment. Structural changes, strain and surface modification introduced in the hydride by high-energy ball milling are found to facilitate desorption. Therefore, ball milling of the materials in the hydrogenated state has been used to reduce the operational desorption temperature. As a result, a remarkable enhancement of hydrogen desorption kinetics has been found for magnesium-based materials. Moreover, ball milling of the mixtures of  $\text{MgH}_2$  and  $\text{Mg}_2\text{NiH}_4$  resulted in a synergetic effect of desorption, allowing the mixture to operate at temperatures of 220–240°C with excellent absorption/desorption kinetics and with total hydrogen capacity exceeding 5 wt.%. This behaviour has been maintained over hydrogenation cycling. In consequence, mechanically treated hydrides offer a new opportunity for magnesium-based materials, exploiting the high capacity of magnesium hydride while operating at much lower temperatures than conventional  $\text{MgH}_2$ .

In a previous paper, we described changes in the microstructure and hydrogenation behaviour of nanocrystalline  $\text{Mg}_2\text{Ni}$  [1] as a result of ball milling. A more recent work [2] analyzed various factors affecting hydriding properties of ball-milled magnesium, in particular the effects of nanocrystalline structure. In the present work, we focused on ball milling of the already formed hydrides of Mg,  $\text{Mg}_2\text{Ni}$  and their mixtures. The effects of structural changes and strain introduced in the Mg-based hydrides by ball milling were studied in connection with their hydrogenation properties, with the aim to compare hydrogenation performance and structural characteristics of Mg-based hydrides in the as-hydrogenated state and after ball milling. More detailed description of the results can be found in Ref. [3].

### **Material fabrication**

In order to study the effects of ball milling on the hydrogenation properties of metal hydrides, firstly the hydrides of Mg and  $\text{Mg}_2\text{Ni}$  were first fabricated. The magnesium powder was hydrogenated in a gas titration system under a hydrogen pressure of 10 bars and at a temperature of 310°C. Completion of hydrogenation was verified by x-ray diffraction to ensure that a single-phase magnesium hydride was obtained. Fabrication of  $\text{Mg}_2\text{Ni}$  was performed by solid-state synthesis, which is an excellent method of production for this difficult intermetallic compound. The process consists of two steps. In the first step, a mixture of appropriate amounts of Mg and Ni is ball milled, in order to obtain a uniform, fine powder of the two intermixed components. In the second stage, the intermixed powders of Mg and Ni are annealed at a temperature high enough to enable the elements to interdiffuse, but low enough to prevent melting of magnesium. In contrast to conventional alloying methods, no evaporation of Mg occurs in this process and the composition can be precisely controlled. Hydrogenation of the

Mg<sub>2</sub>Ni powder (after solid-state synthesis) was performed in a gas titration system. After fabrication, the hydrides of Mg, Mg<sub>2</sub>Ni and their mixtures were subjected to ball milling. A commercial ball mill from Spex (SPEX 8000) was used with stainless-steel vials and stainless-steel balls.

## Results and Discussion

Ball milling is known to change various properties of materials as a result of the formation of special microstructures, metastable phases or modified surfaces. Hydrogenation properties are very sensitive to these modifications and in some cases substantial changes of the hydriding behaviour can be obtained after ball milling. For example, formation of nanocrystalline or amorphous structures produced by ball milling results in dramatic changes in hydrogen sorption properties [4], especially by elimination of the need for activation and improvement of hydriding/dehydriding kinetics. In the present project, studies of mechanical destabilization have focused on high-temperature metal hydrides, i.e. Mg<sub>2</sub>NiH<sub>4</sub> and MgH<sub>2</sub> that have high hydrogen capacity (3.6 wt.% and 7.6 wt.%, respectively) but require high temperature for hydrogen desorption. Properties of the hydrides ball-milled in the hydrogenated state were compared to the hydrides in the as-hydrogenated state as described below.

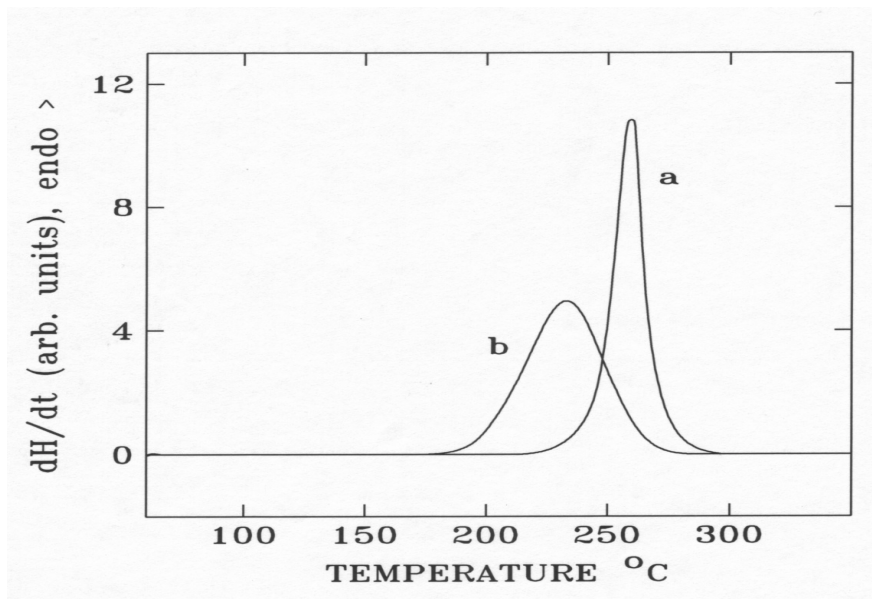
Ball milling of magnesium hydride resulted in a great improvement of hydrogen desorption. The onset of hydrogen desorption is shifted significantly towards lower temperatures after ball milling. Depending on milling time, the onset temperature was reduced by as much as 100°C, and the maximum of the desorption peak was shifted by about 30–50°C. Destabilization of the hydride was also seen in a similar shift of the desorption temperature in the thermogravimetric plots. Measurements in the gas titration system confirmed that magnesium hydride, after ball milling, exhibited excellent kinetics of absorption/desorption. The first dehydrogenation occurred immediately at a temperature between 270 and 280°C. During the subsequent hydrogenation, a full hydrogen capacity of almost 7 wt.% was reached. A key point is that the enhanced kinetics of hydrogenation/dehydrogenation does not disappear after the first hydrogenation, but remains essentially unaltered even after cycling.

P-C-T measurements (performed at 300°C and 330°C) showed that there was no significant shift of the plateau pressure after ball milling of the hydride, which means that there is no substantial difference between the thermodynamic properties of MgH<sub>2</sub> as-hydrogenated and after ball milling. Therefore, the improved performance seems to lie with the kinetics, and does not involve any substantial change of the chemical bonding between magnesium and hydrogen. Amongst kinetic factors, surface modification is one of the most important, because surface properties (low sticking coefficient of hydrogen and the problem of surface oxidation) can seriously limit hydrogenation of magnesium. Ball milling of the hydride can also introduce internal, structural changes such as defects and local imperfections. The broadening of the Bragg peaks confirms the reduction of grain size of the hydride after ball milling, with possibly an additional contribution to the peak width resulting from micro-stress induced in the structure by ball milling.

As for Mg hydride, ball milling of Mg<sub>2</sub>Ni hydride also results in a significant improvement of the kinetics of hydrogen sorption (Figure 1). It was found that after ball milling, reduction of the desorption temperature occurred for both structural modifications of Mg<sub>2</sub>Ni hydride, i.e. the hydride formed at low temperature (180°C) and the hydride formed at high temperature (260°C). After ball milling, Mg<sub>2</sub>NiH<sub>4</sub> desorbed hydrogen even at temperatures as low as 180°C with a desorption time of less than 1h. Structural changes of ball milled Mg<sub>2</sub>NiH<sub>4</sub> were monitored by x-ray diffraction and transmission electron microscopy. These changes most probably involve both reduction of the grain size and formation of a variety of defects.

Even more remarkable improvements of the hydrogenation performance were observed when mixtures of MgH<sub>2</sub> + Mg<sub>2</sub>NiH<sub>4</sub> were ball milled together, after being separately hydrogenated. Various compositions have been studied and the best results were obtained for a composition of 65 wt.% of MgH<sub>2</sub> and 35 wt.% of Mg<sub>2</sub>NiH<sub>4</sub>, as described below. This composition provides a high

capacity of hydrogen (nominally 6.2 wt%), as a result of the large amount of magnesium hydride. Figure 2 shows DSC scans for the mixture of  $\text{MgH}_2 + \text{Mg}_2\text{NiH}_4$  before and after ball milling. For the as-hydrogenated hydrides, two separate endothermic peaks corresponding to hydrogen desorption were observed - a low-temperature peak for  $\text{Mg}_2\text{NiH}_4$  and a high-temperature peak for  $\text{MgH}_2$ . The heat of desorption of  $\text{MgH}_2$  was larger than that of  $\text{Mg}_2\text{NiH}_4$ , both because of the larger amount of  $\text{MgH}_2$  in the mixture, and also because of the larger heat of dissociation of magnesium hydride. After ball milling the mixture, the DSC plot changed remarkably. The peak corresponding to desorption of  $\text{MgH}_2$  totally disappeared and instead a much larger peak was observed at temperatures characteristic for desorption of  $\text{Mg}_2\text{NiH}_4$ . The behaviour observed in the DSC plots suggests that ball milling a mixture of  $\text{MgH}_2$  and  $\text{Mg}_2\text{NiH}_4$  destabilizes the magnesium hydride in such a way that it desorbs hydrogen at temperatures at which only  $\text{Mg}_2\text{NiH}_4$  would normally desorb. Thermogravimetric analysis confirmed this behaviour, as shown in Figure 3. Plot 3(a) represents hydrogen desorption of the untreated mixture of  $\text{MgH}_2$  and  $\text{Mg}_2\text{NiH}_4$ , with separate desorption steps for the two hydrides. The low-temperature step represents desorption of  $\text{Mg}_2\text{NiH}_4$  (which released about 1 wt.% of hydrogen) and the high-temperature effect is attributed to desorption of  $\text{MgH}_2$ . Total hydrogen desorption of the mixture reached about 5.8 wt.%. After ball milling, the mixture behaved in a way parallel to that observed in the DSC scans. Instead of two separate desorption steps, the whole mixture released hydrogen in a single process, and at lower temperatures (Figure3, plot b). Plot 3(c) shows that this behaviour remains reproducible after hydrogenation/dehydrogenation cycling. The fact that magnesium hydride indeed released hydrogen at temperatures as low as 220–240°C was confirmed by x-ray diffraction, which showed no magnesium hydride after desorption at 220°C.



**Figure 1 - Thermal effects of desorption (DSC) for  $\text{Mg}_2\text{NiH}_4$ : a. as-hydrogenated; b. after ball milling (heating rate 10 K/min.).**

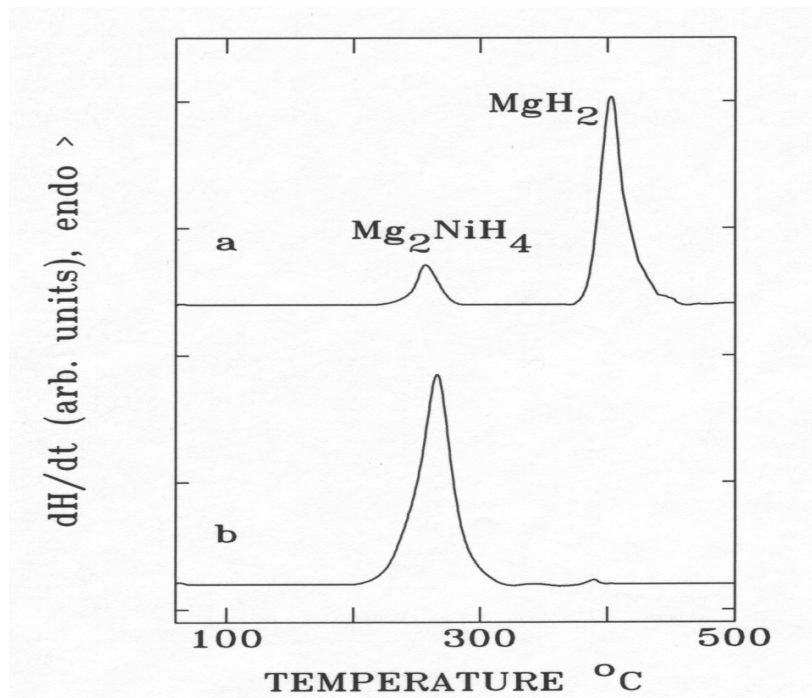


Figure 2 - DSC plots for the mixture of hydrides (65 wt.% of  $MgH_2$  and 35 wt.% of  $Mg_2NiH_4$ ): a. untreated and b. after ball milling for 30min. (heating rate 10 K/min).

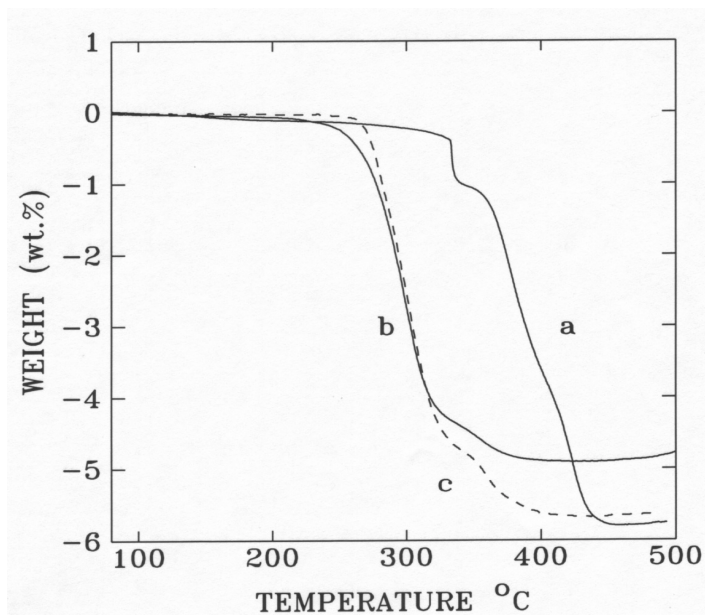


Figure 3 - Thermogravimetric plots (TGA) for the mixture of hydrides (65 wt.% of  $MgH_2$  and 35 wt.% of  $Mg_2NiH_4$ ): a. untreated; b. after ball milling for 30 min.; c. after 15 cycles in gas titration system (heating rate 10 K/min).

Hydrogenation experiments also confirmed the above behaviour and showed that it was fully reproducible over several hydriding/dehydriding cycles (more than 20). Ball milled mixtures of  $MgH_2$  and  $Mg_2NiH_4$  exhibited excellent kinetics during cycling (Figs. 4 and 5).

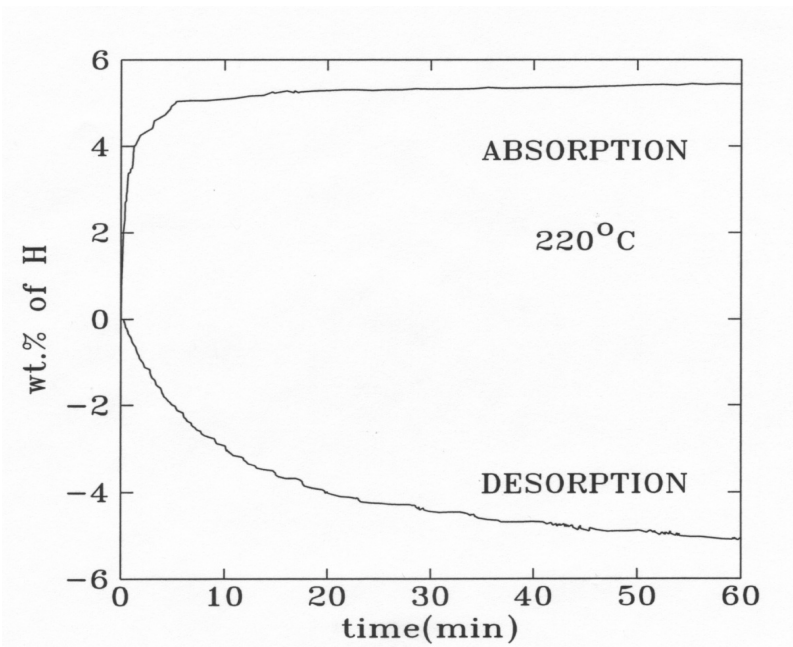


Figure 4 - Rate of absorption and desorption at 220°C for the mixture of hydrides (65 wt.% of  $MgH_2$  and 35 wt.% of  $Mg_2NiH_4$ ) after ballmilling.

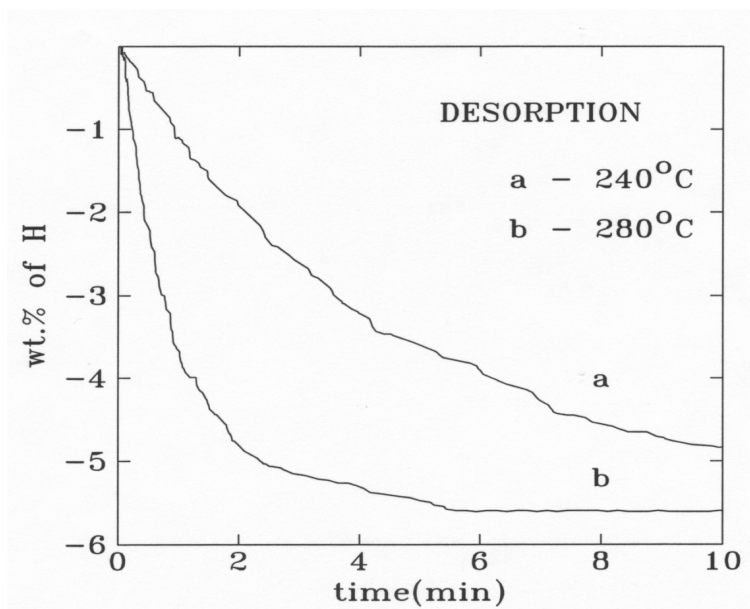


Figure 5 - Rate of desorption at 240°C and at 280°C for the mixture of hydrides (65 wt.% of  $MgH_2$  and 35 wt.% of  $Mg_2NiH_4$ ) after ballmilling.

At temperatures of 240–280°C, absorption and desorption occurred within minutes. Even at 220°C, absorption is completed within about 5 min. and desorption within about 60 min., as shown in Figure 4. It is important to stress that the excellent hydrogenation properties of the mixtures of MgH<sub>2</sub> and Mg<sub>2</sub>NiH<sub>4</sub> were reproducible and did not deteriorate upon cycling (at least up to 20 cycles).

P-C-T measurements of the mixtures showed no *essential* difference in the plateau pressures before and after ball milling. For the untreated mixture, two distinct plateaus can be seen in the isotherm (the higher one for Mg<sub>2</sub>NiH<sub>4</sub> and the lower one for MgH<sub>2</sub>). After ball milling, the intermediate region between the two plateaus becomes less well defined, while the plateau for Mg<sub>2</sub>NiH<sub>4</sub> develops a small slope and the equilibrium pressure for magnesium is marginally increased. The improved performance of the hydride mixtures after ball milling should thus be attributed to modifications in kinetics rather than to substantial changes in thermodynamics. We suggest that the enhancement of kinetics (in particular for hydrogen desorption) is caused by a combination of surface modification and structural imperfections resulting from ball milling.

## Conclusions

It has been found that ball milling of magnesium-based hydrides results in a substantial decrease of desorption temperature, both for MgH<sub>2</sub> and for Mg<sub>2</sub>NiH<sub>4</sub>. Depending on the ball milling conditions, the shift of the onset of desorption temperature can be as large as 100°C for MgH<sub>2</sub> and 40°C for Mg<sub>2</sub>NiH<sub>4</sub>. More interestingly, ball-milled mixtures of MgH<sub>2</sub> and Mg<sub>2</sub>NiH<sub>4</sub> exhibit a synergetic effect of hydrogen sorption that results in excellent kinetic properties of the composite material. For example, a sample of ball milled mixture of 65 wt.% of MgH<sub>2</sub> and 35 wt.% of Mg<sub>2</sub>NiH<sub>4</sub> desorbs hydrogen quickly at temperatures around 220–240°C with hydrogen capacity exceeding 5 wt.%. This result is remarkable in that the dissociation of magnesium hydride does not normally occur at temperatures below at least 300°C. Moreover, the hydrogen desorption/absorption cycling showed that this effect was quite reproducible and did not deteriorate upon cycling. It can be concluded that mechanically treated hydride mixtures offer a new opportunity for magnesium-based materials that take advantage of the high capacity of magnesium hydride and operate at much lower temperatures than conventional magnesium.

## References

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