

H-sorption in MgH₂ nanocomposites containing Fe or Ni with fluorine

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Received 14 June 2004; received in revised form 29 December 2004; accepted 4 January 2005

Available online 11 July 2005

Abstract

Ball milling techniques were used to introduce both fluorine and catalytic transition metals (Fe, Ni) into MgH₂ nanograined powders. XRD was carried out to follow the structural evolution upon milling, whereas the thermal stability against H-desorption was investigated by DSC and TG analysis. The latter showed that fluorine additions with the Fe catalyst effectively decrease the desorption temperature to about 500 K. Results on the absorption/desorption kinetics, which was investigated by volumetric techniques, are presented and discussed with respect to both the simultaneous catalytic activity of Fe or Ni with F and the effect of solid-state processes which may occur upon mechanical alloying. © 2005 Elsevier B.V. All rights reserved.

Keywords: Hydrogen storage materials; High-energy ball milling

1. Introduction

Magnesium hydride is considered as one of the most attractive candidate materials for hydrogen storage, due to its high capacity (about 7.6 wt.%) and low cost. Yet, it exhibits, even at high temperatures, a slow absorption and desorption kinetics, which, up to now, has severely limited any practical application [1]. Many investigations have, therefore, focused on improving the reaction kinetics by both tailoring the MgH₂ microstructure and adding a proper catalyst. For instance, it has been shown [2] that processing MgH₂ by high-energy ball milling techniques is beneficial, as fresh and clean surfaces are created at each impact and different kind of crystalline defects are introduced in the lattice. At the same time, MgH₂ grains are reduced to nanometer scale, the resulting path for hydrogen bulk diffusion within the material being significantly shortened. Ball milling has been also used for producing nano-composites in which MgH₂ is blended with transition metals (e.g. V, Ti, Fe, and Ni) [3] or transition metal oxides, such as Nb₂O₅ or V₂O₅ [4]. In such cases, the metallic or metallic oxide particles are reported to effectively act

as catalysts, fast hydrogen-sorption kinetics being achieved. Improved kinetics has been also reported when Mg-Ni eutectic alloys undergo a fluorination treatment in aqueous solution [5]. For the latter, it is argued that the formation of a fluorinated surface layer enhances hydrogen reactivity and protects the material from passivation.

In this paper, we report on preliminary results for ball-milled MgH₂-nanocomposites containing FeF₃ or NiF₂, which were chosen in order to combine the catalytic effect of transition metals with the possible benefits of fluorinated compounds [6].

2. Experimental

Ball milling was performed in a Fritsch Pulverizette P0 using hardened steel balls and vials. The starting powders (MgH₂ from Sigma-Aldrich, 90% purity, the rest being magnesium; FeF₃ anhydrous from Alfa Aesar, 97% purity; and NiF₂ anhydrous from Strem Chemicals, 99% purity) were charged in the vials in order to have powder mixtures consisting of either MgH₂ + 5 mol% FeF₃ or MgH₂ + 5 mol% NiF₂. The total amount of the starting mixture charged in each vial resulted in a ball-to-powder weight ratio, which

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exceeded 20:1. The milling time was in each case 48 h. All the powder handling before and after milling was carried out in a glove box under a protecting argon atmosphere.

Structural characterization was performed by X-ray diffraction (XRD) analysis using a Siemens D501 equipped with Cu K α radiation in a $\theta/2\theta$ configuration and by transmission electron microscopy (TEM) using a Jeol 3010 operating at 300 keV. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried isochronally (10 K/min) under a constant flow of He in a Netzsch Simultaneous Thermal Analyzer STA 409 equipped with a TASC 414/2 controller. Hydrogen sorption kinetics was investigated at 573 K under vacuum or 10 bar hydrogen during desorption and absorption, respectively. The measurements were performed at GKSS using a volumetric Sieverts-type apparatus designed by Hydro Quebec/HERA Hydrogen Storage Systems.

3. Results and discussion

Fig. 1 shows the XRD patterns (Cu K α) for the MgH₂ powders ball milled for 48 h with FeF₃ (pattern a) or NiF₂ (pattern c). In the case of FeF₃-containing powders, the most intense Bragg peaks that can be observed in the XRD pattern can be identified as coming from the starting materials, i.e. tetragonal MgH₂ (PDF 12-0697) and FeF₃ (PDF 33-0647). Also in the XRD pattern for the NiF₂-containing powders (pattern b of Fig. 1), the most intense peaks are those of the

starting materials, although NiF₂ reflections (PDF 24-0791) are not readily recognized due to an overlapping with MgH₂. In both patterns, additional reflections from MgO (PDF 45-0946) and γ -MgH₂ (PDF 35-1184) can be observed, as well. The latter is a metastable orthorhombic phase, which has been previously reported to form upon milling of MgH₂ [6]. As for the presence of magnesium oxide, this is likely due to slight oxygen contamination. It is worth noticing that Fe reflections (PDF 6-0696) are detected in the pattern for MgH₂ + 5 mol% FeF₃. It can be argued that this could be the result of impurities from milling debris. If that were the case, a comparable amount of iron impurities would be expected to be present also in the NiF₂-containing powders, the milling conditions being the same for both systems. Yet, no iron peaks can be observed in pattern c of Fig. 1. Thus, the small quantity of iron detected in the as milled MgH₂ + 5 mol% FeF₃ powders likely stems from FeF₃.

XRD analysis suggests that, besides the formation of limited amounts of γ -MgH₂ and Fe from FeF₃, the milling process does not induce any clear phase transformation or solid-state reaction. On the other hand, the peak broadening which can be observed in both patterns of Fig. 1 clearly points out that, upon milling, strain and structural defects are introduced into MgH₂. At the same time, the grain size is significantly reduced and can be estimated to be in the nanometer range. This is confirmed by TEM investigations (not shown), which show that the grain size of MgH₂ ranges from about 100 nm to few tens of nanometers. It should be mentioned that much smaller crystallite sizes, e.g. less than 20 nm, have been reported for MgH₂ milled using milling devices and conditions which are different from those used in this work [7].

Constant-heating DSC and TG analysis were carried out in order to investigate the catalytic effect of FeF₃ and NiF₂ additions on the MgH₂ desorption reaction. In Fig. 2, the DSC traces for as-milled MgH₂ + 5 mol% FeF₃ and MgH₂ + 5 mol% NiF₂ are compared with that for pure MgH₂

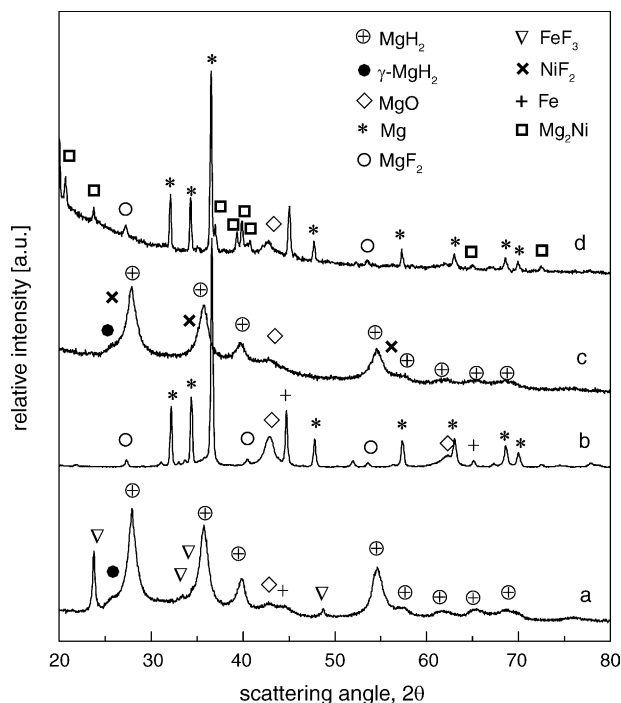


Fig. 1. XRD patterns (Cu K α) for (a) MgH₂ + 5 mol% FeF₃ and (c) MgH₂ + 5 mol% NiF₂ ball milled for 48 h. Results for (b) MgH₂ + 5 mol% FeF₃ and (d) MgH₂ + 5 mol% NiF₂ after DSC/TG analysis are also shown for comparison.

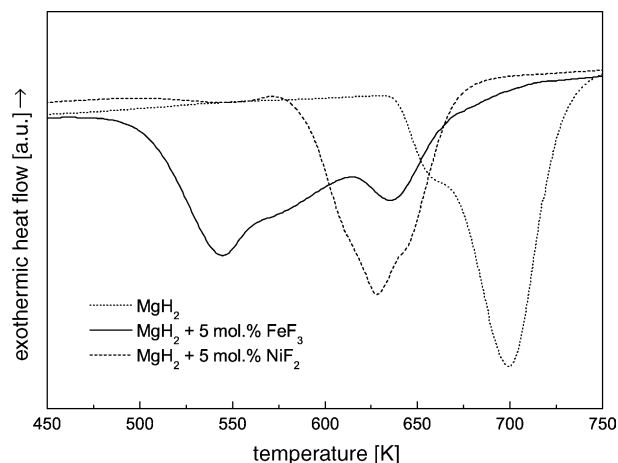


Fig. 2. Constant-heating (10 K/min) DSC trace for MgH₂ + 5 mol% FeF₃ (solid line), MgH₂ + 5 mol% NiF₂ (dashed line), and MgH₂ (dotted line) ball milled for 48 h.

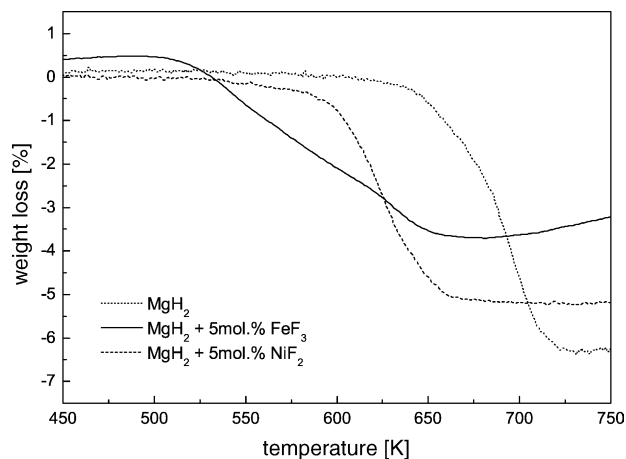


Fig. 3. Thermogravimetric analysis for $\text{MgH}_2 + 5 \text{ mol\% FeF}_3$ (solid line), $\text{MgH}_2 + 5 \text{ mol\% NiF}_2$ (dashed line), and MgH_2 (dotted line) ball milled for 48 h.

powders ball milled for 48 h under the same experimental conditions—i.e. having the same grain size and with no impurities being detected by XRD. The onset of desorption, which is around 640 K for as-milled MgH_2 powders, decreases significantly for the FeF_3 - and NiF_2 -containing powders. For $\text{MgH}_2 + 5 \text{ mol\% NiF}_2$, desorption starts well below 600 K, whereas, for $\text{MgH}_2 + 5 \text{ mol\% FeF}_3$, it begins at about 500 K. On the other hand, it should be noticed that, especially for the FeF_3 -containing powders, the desorption reaction is characterized by several endothermic events and appears to occur over a rather broad temperature range. This can be ascribed to the broad distribution of grain sizes which has been observed by TEM for $\text{MgH}_2 + 5 \text{ mol\% FeF}_3$, and which, in turn, results in different activation energies for hydrogen desorption. TG analysis (see Fig. 3) confirms that the endothermic peaks observed in Fig. 2 stem from the hydrogen desorption reaction and are associated to a weight loss of more than 6% for ball-milled MgH_2 , more than 5% for $\text{MgH}_2 + 5 \text{ mol\% NiF}_2$, and about 4% for $\text{MgH}_2 + 5 \text{ mol\% FeF}_3$. Such values for the weight loss are lower than what one would expect from the theoretical capacity for MgH_2 (about 7.6 wt.%). This can be explained by taking into account the purity of the starting magnesium hydride powder (90%, the rest being Mg), the slight oxidation of the powders, and the relative content of FeF_3 (18.4 wt.%) or NiF_2 (16.2 wt.%), which all contribute in lowering the total capacity of the systems investigated in this work.

The XRD patterns carried out on $\text{MgH}_2 + 5 \text{ mol\% FeF}_3$ and $\text{MgH}_2 + 5 \text{ mol\% NiF}_2$ powders after the DSC/TG runs are shown in Fig. 1 (patterns b and d, respectively). In both cases, it can be seen that MgH_2 has completely transformed into Mg (PDF 35-0821). At the same time, no peaks from the starting catalysts can be detected, whereas reflections from MgF_2 (PDF 41-1443), Fe (PDF 6-0696) (only in pattern b) and Mg_2Ni (PDF 35-1225) (only in pattern d) can be observed. This suggests the occurrence, apparently above the desorption temperature, of a displacement reaction between

Mg and the catalyst. In one case, Mg reacts with FeF_3 to give MgF_2 and Fe, whereas the reaction between Mg and NiF_2 results in the formation of MgF_2 and Mg_2Ni .

The formation of a MgF_2 surface layer has previously been reported for a Mg_2Ni alloy, which underwent a F-treatment in aqueous solution [8]. In that case, the authors argued that the formation of such layer, which exhibits a high affinity to hydrogen, is decisive for a rapid initial activation of the alloy. On the other hand, the formation of magnesium fluoride has already been observed directly upon milling of MgH_2 and FeF_3 , in a planetary ball milling device [6,9]. For the systems investigated in this work, magnesium fluoride is not detected by XRD in the as-milled powders. However, its formation at the $\text{FeF}_3/\text{MgH}_2$ or $\text{NiF}_2/\text{MgH}_2$ interfaces, which are created during the repeated fracturing and cold-welding processes occurring upon milling, cannot be ruled out. Indeed, the presence of limited amounts of iron in the as-milled FeF_3 -containing powders, could be indicative of the mechanically driven solid-state reaction between FeF_3 and MgH_2 to give MgF_2 and Fe. The presence, even in small quantities, of MgF_2 may catalyze the hydrogen desorption, thus explaining the decrease of the desorption temperatures observed for $\text{MgH}_2 + 5 \text{ mol\% FeF}_3$ and $\text{MgH}_2 + 5 \text{ mol\% NiF}_2$, with respect to ball-milled MgH_2 . As the hydrogen desorption reaction proceeds and more Mg is available, more MgF_2 is formed, further favoring the desorption of hydrogen. Of course, such a picture must be substantiated by more evidences and further investigations are currently being performed to clarify the possible role that MgF_2 might play.

It could also be argued that the decrease of the desorption temperature observed for $\text{MgH}_2 + 5 \text{ mol\% FeF}_3$ is simply due to the Fe, which is formed either upon milling or desorption and which has been reported to exhibit a fairly good catalytic activity [3]. However, when MgH_2 and Fe are milled under the same processing conditions used in this work, the resulting powders do not show the marked decrease of the desorption temperature observed for the MgH_2 - FeF_3 composite powders [9]. Therefore, although it likely contributes significantly to the overall sorption behavior, Fe cannot be, in our case, the sole responsible for the improved desorption.

Finally, preliminary investigations on the H-sorption kinetics have been carried out to further estimate the catalytic activity of the fluoride additions and to test the effect of cycling. Fig. 4 shows the two consecutive runs for desorption (at 573 K under vacuum) and absorption (at 573 K under 10 bar hydrogen) as measured for the as-milled $\text{MgH}_2 + 5 \text{ mol\% FeF}_3$ system. It can be seen that, during the first desorption run, 4 wt.% of hydrogen is desorbed already after 600 s, whereas the same amount is desorbed after less than 500 s during the second run. As for the absorption, for both runs, it is complete after about 1200 s, the hydrogen uptake being slightly faster during the second run. This clearly indicates that, at least after one cycle, the H-sorption behavior not only is preserved, but it actually improves. A much faster kinetics have previously been reported for $\text{MgH}_2 + 5 \text{ at.\% V}$ [10] and for $\text{MgH}_2 + 0.5 \text{ mol\% Nb}_2\text{O}_5$ [4]. Nonetheless, our

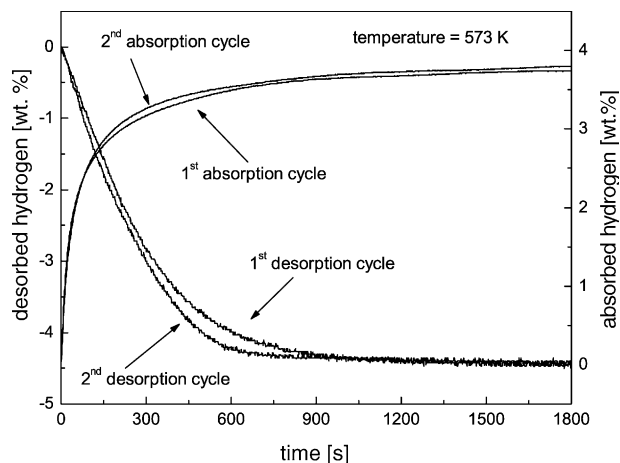


Fig. 4. Sorption kinetics for as-milled $\text{MgH}_2 + 5 \text{ mol\% FeF}_3$ at 573 K. Desorption was carried out under vacuum, whereas absorption was performed under 10 bar hydrogen.

results can be regarded as very promising, if one considers that the grain size for the as milled powders is not homogeneous, as mentioned above few grains being larger than 100 nm. A significant improvement in the sorption kinetics should be expected if the milling parameters are adjusted and homogeneous grain sizes, in the order of about 20 nm, are achieved.

4. Conclusions

Ball milling techniques were used to produce MgH_2 nanocomposites containing FeF_3 and NiF_2 . It was shown that fluoride additions are beneficial, with respect to the H-sorption behavior. In the case of FeF_3 additions, the desorp-

tion temperature, as measured by isochronal DSC (10 K/min), is as low as 500 K and the time necessary for H-desorption after one cycle at 573 K is less than 500 s. Further investigations are required to clarify the catalytic role played by MgF_2 , the latter being formed during desorption.

Acknowledgements

The authors would like to thank D. Foscallo for technical assistance and J.F.R. de Castro for stimulating and fruitful discussions. This work was supported by the EU Research and Training Network HPRN-CT-2002-00208 coordinated by A.R. Yavari. W.J. Botta would also like to acknowledge CNPq, Brazil, for a research grant.

References

- [1] L. Schlapbach, A. Züttel, *Nature* 414 (2001) 353.
- [2] A. Zaluska, L. Zaluski, J.O. Strom-Olsen, *J. Alloys Compd.* 288 (1999) 217.
- [3] G. Liang, J. Huot, S. Boily, A. Van Neste, R. Schultz, *J. Alloys Compd.* 292 (1999) 247.
- [4] G. Barkhordarian, T. Klassen, R. Bormann, *Scripta Mater.* 49 (2003) 213.
- [5] F.-J. Liu, S. Suda, *J. Alloys Compd.* 231 (1995) 742.
- [6] A.R. Yavari, J.F.R. de Castro, T.T. Ishikawa, W.J. Botta, Patent PI0305917-0 (2003), Brazil.
- [7] J. Huot, G. Liang, S. Boily, A. Van Neste, R. Schultz, *J. Alloys Compd.* 293–295 (1999) 495.
- [8] F.-J. Liu, S. Suda, *J. Alloys Compd.* 232 (1996) 212.
- [9] J.F.R. de Castro, A.R. Yavari, A. LeMoulec, T.T. Ishikawa, W.J. Botta, *J. Alloys Compd.* 389 (2005) 270.
- [10] G. Liang, J. Huot, S. Boily, R. Schultz, *J. Alloys Compd.* 305 (2000) 239.