

Journal of ALLOYS AND COMPOUNDS

Journal of Alloys and Compounds 432 (2007) L1–L4

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Letter

Improving hydrogen sorption kinetics of MgH₂ by mechanical milling with TiF₃

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Received 24 April 2006; received in revised form 25 May 2006; accepted 25 May 2006

Available online 7 July 2006

Abstract

 $MgH_2 + TiF_3$ system was mechanically prepared and investigated with regard to hydrogen absorption/desorption performance. It was found that the sorption kinetics of MgH_2 can be markedly improved by mechanical milling with 4 mol% TiF₃, in particular at reduced operation temperatures. Even at a moderate temperature range (313–373 K), the hydrogen absorption can be largely completed within about 25 s. On the desorption aspect, the catalytic enhancement arising upon adding TiF₃ allows the sample to desorb near 5 wt.% hydrogen within 600 s at 573 K. Furthermore, such enhancement in kinetics was observed to persist in the absorption/desorption cycles. Preliminary XRD examination was also performed to understand the observed catalytic effect of TiF₃ additive.

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Keywords: Magnesium; Hydrogen storage; Kinetics; TiF3

1. Introduction

As a hydrogen storage medium, MgH₂ is highly appreciated due to its high hydrogen capacity and low cost. However, the practical application of MgH₂ for onboard hydrogen storage is largely hampered by its high thermodynamic stability and sluggish sorption kinetics [1]. After decades of extensive research efforts, partial success has been achieved in improving the kinetic performance of MgH₂ while leaving the problematic thermodynamics untouched. It was found that the addition of Hstorage alloys, transition metals and/or their oxides, fluorides, and even some non-metal materials through mechanical milling might all accelerate the absorption/desorption processes of magnesium [2-26]. However, most of the literature reports focus on the property improvement at relatively high temperatures (usually higher than 473 K). Only few reports concern the substantial kinetics improvement at a moderate operation temperature lower than 373 K, which is of practical interests for onboard H-storage application. Liang et al. claimed that the mechanically prepared MgH₂ + 5 mol%Ti and MgH₂ + 5 mol%V systems exhibited rapid absorption kinetics at temperatures ranging from room temperature to 373 K [27,28]. Hanada et al. reported that, by

0925-8388/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2006.05.103 mechanical milling MgH_2 with a small amount of mesoporous Nb_2O_5 , more than 5 wt.% hydrogen could be restored within 30 s at 423 K. What is more striking, about 4.5 wt.% hydrogen could be absorbed within 15 s even at room temperature [29].

Quite recently, in our investigation on sodium alanate system, we found that TiF_3 possessed pronounced catalytic effect on the reversible de-/hydrogenation of NaAlH₄. In comparison with the conventional TiCl₃, this novel dopant precursor resulted in further enhanced H-capacity, de-/hydriding kinetics as well as reduced operation temperature and pressure conditions [30–32]. Interestingly, in the study of Mg-based materials, it has been demonstrated that both Ti hydride and F⁻ contribute to the catalytic enhancement of the absorption/desorption processes of MgH₂ [12,24,25,27]. As a source of both species, TiF_3 is therefore of great interest for preparing catalytically enhanced Mg-based H-storage materials.

In the present study, the $MgH_2 + TiF_3$ system was mechanically prepared and examined with respect to hydrogen sorption kinetics. As expected, this system possesses enhanced sorption kinetics, in particular the absorption performance at a moderate temperature range.

2. Experimental

The starting material MgH₂ was prepared by mechanical milling magnesium powder (purity >99.9%, 300 mesh) under hydrogen atmosphere with an

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initial pressure of ~1 MPa, followed by hydrogenation for 12 h at 623 K. The process was repeated for three times to achieve a hydrogenation ratio of ~80%, as determined by using the volumetric method [26]. The TiF₃ powder was purchased from Sigma–Aldrich Chemical Corp. and was used as received. The MgH₂ + 4 mol%TiF₃ mixture was mechanically milled under Ar atmosphere for 10 h by using a Fritsch P7 planetary mill with stainless steel vial and balls at 400 rpm. The ball-to-powder weight ratio was about 40:1. For comparison, MgH₂ was mechanically milled under identical conditions. All the sample handling was performed in an Ar-filled glove-box equipped with purification system, in which the typical H₂O/O₂ levels are below 1 ppm.

The samples were characterized by X-ray diffraction (XRD, Rigaku D/max 2400) with Cu K α radiation. Hydrogen storage properties of the samples, with a typical amount of around 200 mg, were examined by using a carefully calibrated Sievert-type apparatus. Absorption/desorption measurements were performed at desired temperatures with an initial hydrogen pressure of 2.0 and 0.01 MPa, respectively. The hydrogen supply (with an initial purity of 99.999%) was further purified by using a hydrogen storage alloy system to minimize H₂O/O₂ contamination. To allow a practical evaluation of the hydrogen storage capability of the materials, the weight of the catalyst was taken into account in the determination of H-capacity.

3. Results and discussion

Mechanical milling with TiF₃ has resulted in marked improvement on the absorption kinetics of Mg. As seen in Fig. 1, the sample with 4 mol% TiF₃ additive could absorb 5 wt.% hydrogen within about 30 s at 573 K, with an average absorption rate 20 times higher than that of pure Mg. Moreover, in great contrast to the high kinetics-temperature dependence in pure Mg, the variation of operation temperature from 573 to 423 K was observed to produce no detectable influence on the absorption kinetics of MgH₂ + 4 mol%TiF₃. Within the investigated period, the only effect of lowered temperature was that the Hcapacity decreased from over 5 wt.% at 573 K to about 3.8 wt.% at 423 K. Here it should be noted that the samples with TiF₃ additive exhibited their optimal H-absorption/desorption performance from the 1st cycle, thus eliminating the pre-activation generally required for pure Mg.

Of particular interest, it was found that the fast absorption kinetics of the sample milled with TiF_3 was well maintained



Fig. 1. Hydrogen absorption curves (with an initial hydrogen pressure of 2.0 MPa) of mechanically milled $MgH_2 + 4 \mod\% TiF_3$ and MgH_2 at varied temperatures: (a) 573 K, (b) 473 K and (c) 423 K for $MgH_2 + 4 \mod\% TiF_3$; (d) 573 K and (e) 473 K for MgH_2 .



Fig. 2. Hydrogen absorption curves of $MgH_2 + 4 \mod\% TiF_3$ at moderate temperatures: (a) 373 K, (b) 340 K, and (c) 313 K.

at moderate temperature. As shown in Fig. 2, even at 313 K, about 2 wt.% hydrogen could be recharged within 25 s. When the operation temperature was increased to 373 K, the restored hydrogen amount within 25 s increased to 3.4 wt.%. Such kinetic performance is comparable to the highest level of the literature results [27–29].

The pronounced catalytic enhancement arising upon adding TiF₃ was also observed on the H-desorption aspect. Fig. 3 gives the typical H-desorption curves of the MgH₂ samples with and without TiF₃ additive at varied temperatures. For the pure MgH₂ sample, appreciable H-desorption could be achieved only when the operation temperature was increased up to 623 K (curve c). While for the MgH₂ + 4 mol%TiF₃ sample, near 5 wt.% hydrogen was desorbed within 600 s at 573 K (curve e). Even at a lowered temperature of 553 K, the sample with TiF₃ additive could release about 2.8 wt.% hydrogen within 600 s, much faster than that of pure MgH₂ at 623 K. Currently, without definite evidence on the favorable thermodynamic adjustment, the observed accelerated desorption rate and reduced operation temperature



Fig. 3. Hydrogen desorption curves of $MgH_2 + 4 \text{ mol}\%\text{TiF}_3$ and MgH_2 at varied temperatures with an initial H-pressure of 0.01 MPa: (a) 573 K, (b) 593 K, and (c) 623 K for MgH_2 ; (d) 553 K, (e) 573 K for $MgH_2 + 4 \text{ mol}\%\text{TiF}_3$.



Fig. 4. Hydrogen absorption/desorption curves of $MgH_2 + 4 \mod\% TiF_3$ in the 1st and 16th cycle at 573 K.

are attributed to kinetic improvement arising upon adding TiF_3 . Further investigations on the thermodynamic properties (i.e. pressure–composition–isotherms measurements) of the materials are therefore required to clarify this point.

The mechanically prepared MgH₂ + 4 mol%TiF₃ was further examined with respect to the cycling performance. Whereas the materials possess fast kinetics at moderate temperature, an operation temperature of 573 K was applied in absorption/desorption cycles to evaluate the performance stability at elevated temperature [33]. As seen in Fig. 4, the absorption/desorption kinetics persisted well even after 15 cycles. However, the hydrogen capacity was observed to gradually decrease, and down to 4.6 wt.% in the 16th cycle within the investigated timescale. Fortunately, further investigation has found that the problematic capacity loss upon cycling could be partially solved by adjusting the composition of the system, the details of which will be presented in a forthcoming paper.

In our preliminary efforts to understand the catalytic effect of TiF₃ on the sorption kinetics of MgH₂, XRD examination was performed. Fig. 5 presents the XRD patterns of the asmilled MgH₂ + 4 mol%TiF₃ sample as well as those after dehydrogenation and hydrogenation at 573 K. For comparison, the profile of the pure MgH₂ sample milled under identical conditions is also included. It was observed that the diffraction patterns of the as-milled samples with or without TiF₃ additive were quite similar. Both were characterized by the weak and broad diffraction peaks, indicating the decreased grain size and the increased lattice strain [12,19-21,24,25]. Additionally, the intensive milling led to a partial transformation of MgH₂ from a low-pressure β -phase (tetragonal) to a high-pressure metastable γ -phase (orthorhombic) [7,20,25,26], which disappeared in the following de-/hydrogenation processes. For the asmilled $MgH_2 + 4 \mod\% TiF_3$ sample, no diffraction peaks from TiF₃ or any other reaction products could be definitely identified. But the situation changed after the sample was subjected to de-/hydrogenation processes. As shown in the patterns (c) and (d), MgF₂ and TiH₂ could then be identified. Judging from the thermodynamic potentials of the various possible reaction pathways, the formation of these two phases should follow reaction



Fig. 5. XRD patterns for: (a) as-milled MgH₂, (b) as-milled MgH₂+4 mol%TiF₃, (c) MgH₂+4 mol%TiF₃ after dehydrogenation at 573 K, and (d) MgH₂+4 mol%TiF₃ after hydrogenation at 573 K. A small amount of MgO was detected, which may come from air contamination during XRD measurements.

(1) [34]: $MgH_2 + \frac{2}{3}TiF_3 \rightarrow MgF_2 + \frac{2}{3}TiH_2 + \frac{1}{3}H_2,$ $\Delta_r G_m^{\circ} = -197 \text{ kJ/mol}$ (1)

In view of the instant high-energy environment produced by collision between vial and balls and among the balls, it is highly expected that this reaction can occur, at least partially, during milling process. The failure to detect the *in situ* formed phases in the as-milled samples should be ascribed to the defective nanostructure and the peak locations close to those of host hydride. More exactly, the weak diffraction peaks from the *in situ* formed phases might be masked by large and broad neighboring peaks of Mg hydride. After being subjected to de-/hydrogenation processes, both the *in situ* formed and host hydride phases obtained an increased structure ordering. As a result, the previously invisible phases became visible, and previously weak peaks became stronger.

The combined property examination and phase characterization suggest a possible correlation between the *in situ* formed MgF₂ and/or TiH₂ and property improvement achieved in the $MgH_2 + 4 mol\%TiF_3$ system. From literature, both phases possess catalytic activity on the absorption/desorption processes of MgH₂. It has been proposed that, in the MgH₂ samples milled with transition metal (Fe, Ni) fluorides, the formed MgF₂ replaces the original surface oxide layer and provides a reactive and protective fluorinated surface for hydrogen uptake [24,25]. Ti species in the catalytic form of titanium hydride were reported to be excellent in enhancing the absorption/desorption kinetics of host MgH₂ among those investigated transition metals [27]. In the present material system, both MgF2 and TiH2 phases were involved. However, the attempt of adding both phases simultaneously into the host MgH2 did not result in a catalytic enhancement similar to that obtained by adding TiF₃, especially at moderate operation temperatures (results not shown here). Therefore, the observed kinetic enhancement should not be safely attributed to the role of MgF₂ and TiH₂ phases (or even a possible synergetic catalytic function of the individual catalysts). This leaves open the question of the dominant catalytic mechanism responsible for the kinetic enhancement. It is worth noting that for the MgH₂ + Nb₂O₅ and MgH₂ + Nb systems, which possess fast Hsorption kinetics at moderate temperatures, a newly identified ternary magnesium–niobium oxide has been suggested to act as a catalytically active phase [16,35]. This finding may provide a ready reference for the current MgH₂ + TiF₃ system. In this regard, further investigations are currently underway.

4. Conclusions

By mechanical milling with TiF₃, the hydrogen sorption kinetics of MgH₂ could be markedly improved, in particular on the absorption half-cycle at near room temperature. Furthermore, the catalytically enhanced kinetic performance was found to persist in the absorption/desorption cycles. But the catalytic mechanism has not yet been well established. In addition, this system still suffered from cycling capacity loss. Further exploration on the composition–structure–property correlation may lead to a comprehensive mechanism understanding and make possible optimal preparation conditions to pursue further improved sorption kinetics and capacity.

Acknowledgements

The financial support for this research from the Hundred Talents Project of Chinese Academy of Sciences is gratefully acknowledged. L. Ma thanks Mr. Cheng-Zhang Wu, Mr. Xiang-Dong Kang and Mr. Yong Chen for their helpful discussions.

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