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Hydrogen desorption kinetics of nanostructured MgH_2 composite materials

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Abstract

In order to investigate the microscopic mechanism of hydrogen desorption we have studied ball-milled magnesium-composite materials with a relatively large volume fraction of additives. After ball milling the microstructure typically shows additive particles covered with a film of MgH_2 as investigated by scanning electron microscopy and energy-dispersive X-ray microanalysis. Depending on the milling time and material used as additive, the desorption of hydrogen takes place at a far lower temperature than in pure MgH_2 as studied by thermal desorption spectroscopy. In the next step we developed a new method to use only small volume fractions of additives in order to minimize the amount of additive material and maximize the percentage of hydrogen storage material. Therefore, MgH_2 was sputter-deposited by palladium and successively ball milled to achieve a composite material with finely dispersed metallic additives. The desorption kinetics could be strongly improved even though only small amounts of palladium were added. The new method of ultra-fine dispersion may lead to MgH_2 composite materials with a high storage capacity of hydrogen accessible at moderate temperatures.

Keywords: Mechanical alloying; Magnesium hydride; Hydrogen storage materials; Thermal desorption spectroscopy

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1. Introduction

The most important parameters of a hydrogen storage material are its storage capacity and its hydrogen desorption temperature. Due to the high storage capacity of 7.66 wt.%[1], MgH_2 is an ideal candidate for hydrogen storage applications. However, absorption of hydrogen in magnesium and desorption of hydrogen from MgH_2 are very slow processes, and require temperatures of about 600 K.

Tanguy et al. [1] showed that the kinetics can be highly improved by adding metallic additives (e.g. $LaNi_5$ or Pd) to MgH_2 and mechanically alloying using ball-milling. During the last 5 years, several groups investigated a large variety of ball-milled magnesium-based composite materials and mainly attributed the improved kinetics to the nanometer-sized grain structures, however, without clarifying the exact atomistic mechanism [2–6]. For the first time, based on detailed scanning electron microscopy (SEM) analysis, Gross et al. [7] proposed two possible microscopic reasons for the improved kinetics in ball-milled magnesium-composite materials: Firstly, the free surface area of magnesium is enlarged by mechanical alloying. Secondly, the additives may act as catalysts, e.g. by dissociating H_2 molecules into H atoms, which can diffuse along the grain boundaries between magnesium and the additive material, and which can be more easily absorbed by magnesium or magnesium compounds than H_2 molecules.

Later on, using ball-milled magnesium-composite materials with a high amount of additives, Reule et al. [8] were able to clarify the catalytic mechanism in a more detailed way. Based on these measurements, we tried to reduce the fraction of additives, however, keeping the microstructure, i.e. the interface area between MgH_2 and the additive similar. Furthermore, such a reduction of additives is essential for any technological application of these composite materials.

2. Experimental details

Firstly, MgH_2 powder (purity: 98 at.%, distributed by ABCR Karlsruhe) was mechanically alloyed with the additives $La(Ni_{0.7}Fe_{0.3})_5$ and $PdFe_3$ using a planetary ball mill (Fritsch Pulverisette) with an agate bowl filled with an argon atmosphere and agate balls at a rotation speed of 585 rpm. The weight fractions of the additives were 85 wt.% for $La(Ni_{0.7}Fe_{0.3})_5$ and 82 wt.% for $PdFe_3$. The micro-

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[1] Metal Hydride Properties Database, http://hydpark.ca.sandia.gov/.

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structure was investigated by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray analysis (EDX). Therefore, powder particles of the ball-milled material were embedded into a Cu/plastic matrix and mechanically polished.

Secondly, palladium was deposited on MgH_2 powder with an ion-beam sputtering device utilizing a filamentless rf-induced ion gun. About 1 g of MgH_2 was homogeneously distributed on an area of 10 570 mm^2 and the thickness of the palladium layer was chosen between 10 and 20 μm corresponding to a palladium content of 14 and 22.5 wt.%, respectively. Then the powder was mechanically alloyed using a stainless steel bowl and balls at a rotation speed of 440 rpm filled with a hydrogen atmosphere of 1.1 MPa. For the milling times 1 and 5 h were chosen.

The different phases in the mechanically alloyed materials were determined by X-ray diffraction (XRD) using a Siemens D5000 diffractometer (Cu Kα radiation, secondary monochromator).

The hydrogen desorption kinetics were measured using thermal desorption spectroscopy (TDS) as described by Mommer et al. [9] with small modifications in order to improve the temperature measurement. The samples were placed into a high vacuum system and could be heated up to 870 K using a radiation furnace. The hydrogen desorbed was detected by a PC-controlled quadrupole mass spectrometer. Several specific properties of the materials can be derived from the TDS measurements: Firstly, the characteristic temperature T_{max} at which the desorption rate reaches its maximum. A high value of T_{max} denotes poor desorption kinetics, a low value of T_{max} good kinetics. Furthermore, the occurance of more than one maximum points to several processes with different desorption kinetics. Finally, the integral of the desorption curve is proportional to the total amount of desorbed hydrogen, i.e. the storage capacity.

3. Experimental results

3.1. Characterization of microstructure

Fig. 1 shows an SEM micrograph of ball milled $MgH_2 + Pd_3Fe$. The very bright spot in the middle was identified as a Pd_3Fe particle by EDX. The surrounding conglomerate of dark grey particles was identified as MgH_2 (Cu and plastic from the matrix are light gray and black, respectively). Similar micrographs were found for all the ball-milled samples with microcrystalline additives. Therefore, after ball milling the microstructure consists of additive particles covered by a film of MgH_2 as schematically shown in Fig. 2.

The XRD spectra of the ball-milled samples show peaks of MgH_2 and the additive. Using a stainless steel bowl instead of agate, peaks of FeNi can be found, additionally. With increasing milling time, all the peaks become smaller and broader which means, that the crystallite sizes become smaller.

3.2. Thermal desorption kinetics

The hydrogen desorption spectra of ball milled MgH_2, $MgH_2 + La(Ni_{0.7}Fe_{0.3})_5$, and $MgH_2 + Pd_3Fe$ are plotted in Fig. 3. For pure ball milled MgH_2 most of the hydrogen

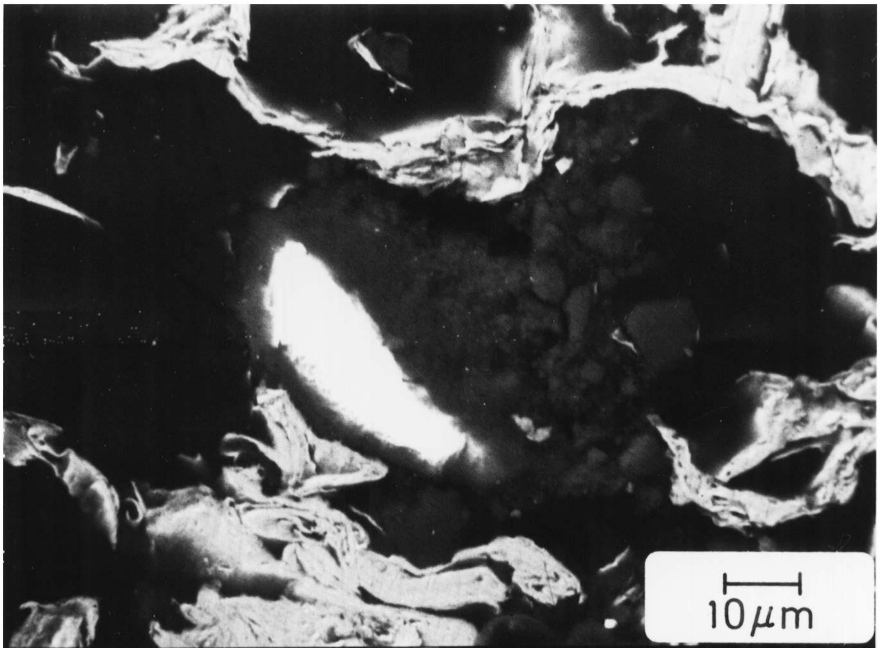

Fig. 1. SEM micrograph of ball milled $MgH_2 + Pd_3Fe$.

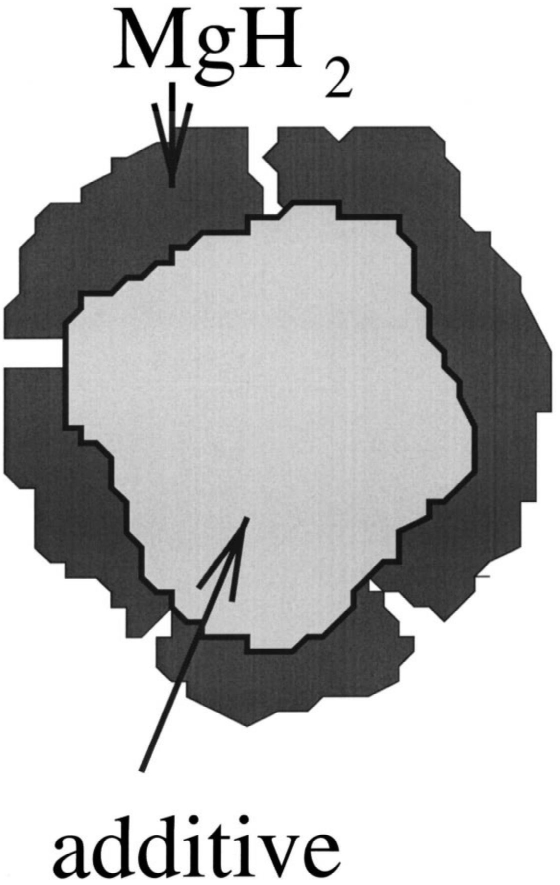

Fig. 2. Schematic cross-sectional view of the microstructure achieved by mechanical alloying of MgH_2 + additive [8].

desorption takes place in the temperature range from 600 K up to 700 K. After ball milling MgH_2 with 85 wt.% $La(Ni_{0.7}Fe_{0.3})_5$, there is another maximum of desorption at 490 K, and after ball milling MgH_2 with 82 wt.% Pd_3Fe, the first maximum of desorption is higher and reaches from 500 K up to almost 580 K.

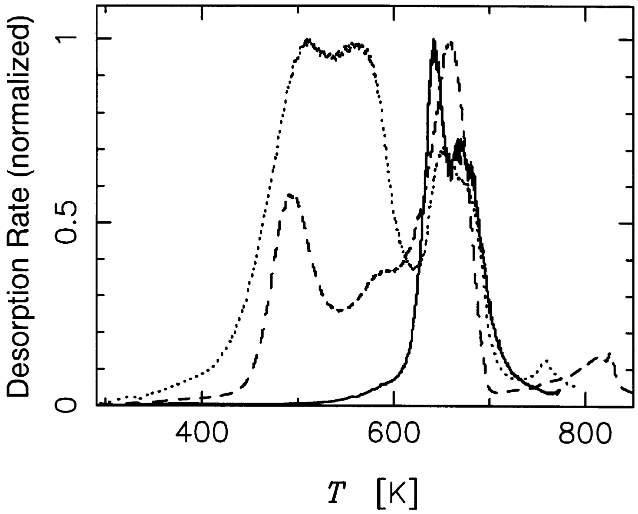

Fig. 3. Hydrogen desorption rates of ball milled MgH_2 (straight), $MgH_2 + La(Ni_{0.7}Fe_{0.3})_5$ (dashed), $MgH_2 + Pd_3Fe$ (dotted), heating rate: 3 K min^{-1}.

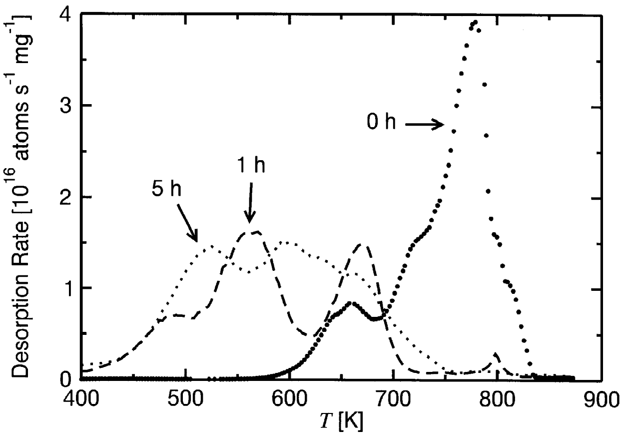

Fig. 4. Hydrogen desorption rate of MgH_2 + 14 wt.% Pd after different milling times (heating rate: 5 K min^{-1}).

The hydrogen desorption rates of MgH_2 with different contents of sputtered palladium are plotted in Fig. 4 (14 wt.% Pd) and Fig. 5 (22.5 wt.% Pd) for different milling times. After sputter-depositing 14 wt.% of palladium on MgH_2, the desorption rate shows two maxima, a small one at 660 K and a large one at 780 K. Most of the hydrogen desorbs above 700 K. After ball milling for 1 h, a broad desorption spectrum appears between 450 and 700 K with two major maxima at 560 and 670 K. The maximum at 670 K is similar to the small one in the material prior to milling. The major part of hydrogen desorbs below 700 K. After 5 h of ball milling a broad spectrum in the same temperature range appears, however, the major desorption maxima are shifted to lower temperatures, i.e. 520 and 590 K.

Prior to milling the sample containing 22.5 wt.% of palladium shows a desorption spectrum with a small maximum at 610 K and a large one at 800 K (Fig. 5). After ball milling for 1 h, similar to the material with 14

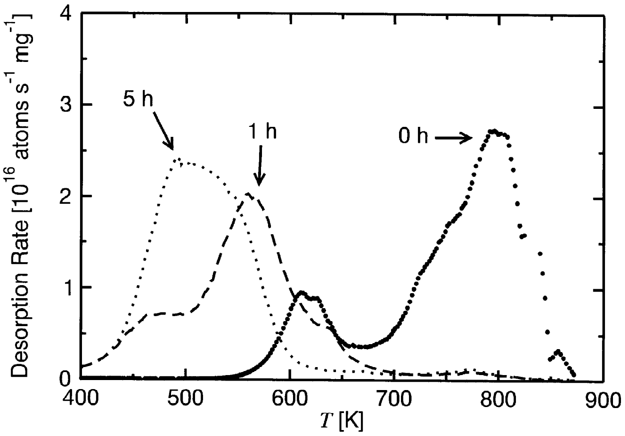

Fig. 5. Hydrogen desorption rate of MgH_2 + 22.5 wt.% Pd after different milling times (heating rate: 5 K min^{-1}).

wt.% of palladium, a broad desorption spectrum in the temperature range from 450 K up to 650 K appears and the desorption above 700 K is negligible. After ball milling for 5 h the hydrogen content desorbs completely in the region between 450 and 600 K.

4. Discussion

As shown in our previous investigations [8], there is no simple correlation between the crystallite sizes and the desorption kinetics of ball-milled MgH_2 with additives. By SEM and EDX analysis we showed that the microstructure of samples which were ball milled with large fractions of microcrystalline Pd_3Fe or $La(Ni_{0.7}Fe_{0.3})_5$ consists of additive particles surrounded by films of MgH_2 (Fig. 2). The main reasons for the improvement of the desorption kinetics are the large interfaces between MgH_2 and additive and its catalytic effect which are formed during ball milling. The importance of the catalytic effect of metal particles was shown by using Si instead of metals, where no improvement in the desorption kinetics was observed [8].

In order to increase the interface area between additive and MgH_2 and in addition to reduce the volume fraction of the additive, we deposited palladium on the MgH_2 powder by ion-beam sputtering. After the MgH_2 powder was covered with a thin palladium layer in the order of several μm the samples were ball milled under H_2 atmosphere to achieve a good mixing. After sputter-depositing palladium on MgH_2 powder the major hydrogen desorption is shifted about 100 K to higher temperatures than in pure MgH_2 powder. Already after ball milling for 1 h this high temperature range disappears, while a new range of high desorption rates from 450 K up to 580 K can be observed which is at lower temperatures than in pure MgH_2 powder. This can be explained by the growing of the interface area between palladium and MgH_2 during ball milling and its catalytic effect. With increasing milling time and increasing palladium content, the fraction of hydrogen desorbing in this low temperature region increases. After 5 h of ball milling with 22.5 wt.% of palladium the maximum desorption rate occurs at 490 K and the total hydrogen content is already desorbed below 600 K. This clearly shows that a large interface area with a catalytic effect on the hydrogen desorption can be achieved with a reduced amount of additives by applying our new technique.

Additionally, the much smaller fraction of additives leads to a higher gravimetric storage capacity of this composite (in the best case shown here 6.0 wt.%) and makes the material attractive for technological applications.

5. Summary

Using ball milled MgH_2 composite materials with high amounts of additives the improved hydrogen desorption kinetics were attributed to a large MgH_2-additive interface with a catalytic effect.

By sputter-depositing palladium on MgH_2 powder and successive ball milling we could significantly decrease the additive content while keeping a large MgH_2-additive interface. The desorption kinetics could even be improved and lowered by more than 150 K compared to pure MgH_2. The large hydrogen storage capacity (6.0 wt.%) of this new finely-dispersed magnesium-composite material showing excellent desorption kinetics around 500 K may be interesting for technical applications.

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References

[1] B. Tanguy, J.-L. Soubeyroux, M. Pezat, J. Portier, P. Hagenmuller, Mater. Res. Bull. 11 (1976) 1441–1447.

[2] L. Zaluski, A. Zaluska, J.O. Ström-Olsen, J. Alloys Comp. 253–254 (1997) 70–79.

[3] S. Orimo, H. Fujii, Intermetallics 6 (1998) 185–192.

[4] M. Terzieva, M. Khrussanova, P. Peshev, J. Alloys Comp. 267 (1998) 235–239.

[5] G. Liang, S. Boily, J. Huot, A. Van Neste, R. Schulz, J. Alloys Comp. 268 (1998) 302–307.

[6] J.-L. Bobet, E. Akiba, Y. Nakamura, B. Darriet, Int. J. Hydrogen Energy 25 (2000) 987–996.

[7] K. Gross, D. Chartouni, E. Leroy, A. Züttel, L. Schlapbach, J. Alloys Comp. 269 (1998) 259–270.

[8] H. Reule, M. Hirscher, A. Weißhardt, H. Kronmüller, J. Alloys Comp. 305 (2000) 246–252.

[9] N. Mommer, M. Hirscher, F. Cuevas, H. Kronmüller, J. Alloys Comp. 266 (1998) 255–259.