

Thermal stability of nanocrystalline magnesium for hydrogen storage

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Abstract

Magnesium hydride is considered to be one of the most interesting alternatives for the reversible storage of hydrogen. It is abundant, inexpensive, easy to handle, environmentally benign and exhibits a high hydrogen storage capacity of up to 7.6 wt.%. Furthermore, nanocrystalline Mg powder prepared by high energy ball milling and the addition of suitable catalysts shows very fast absorption and desorption kinetics. The thermal stability of the nanocrystalline microstructure as well as the respective sorption kinetics of ball-milled MgH_2 with or without 0.5 mol% Nb_2O_5 as catalyst have been investigated after cycling and annealing at the technically relevant temperatures between 300 and 400 °C. While kinetics for pure MgH_2 slows down substantially already after a few cycles at 300 °C, MgH_2 with Nb_2O_5 catalyst still shows fast sorption kinetics after annealing up to 370 °C. At higher temperatures, the kinetics for the catalyzed material also breaks down, which is attributed to a deterioration of the catalyst. Continuous coarsening of the microstructure during annealing leads to an increased fraction of the storage capacity that can only be recharged at a slower rate. This is discussed in terms of retarded growth conditions for the MgH_2 phase. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Hydrogen is the ideal means of energy storage for transportation and conversion of energy in a comprehensive clean-energy concept. However the storage of hydrogen is still a big challenge because of the very low boiling point of hydrogen (20 K at 1 atm) and its low density in the gaseous phase (0.0071 g/cm³). Furthermore the storage in liquid or gaseous form imposes safety problems, in particular for mobile applications. Magnesium hydride is considered to be one of the most interesting alternatives for the reversible storage of hydrogen, because of its high gravimetric hydrogen storage capacity of 7.6 wt.%. Magnesium hydride is environmentally benign, abundant, inexpensive and easy to handle. Very fast kinetics can be reached by the use of high-energy ball milling and the addition of suitable catalysts [1–5]. Fast desorption kinetics have been observed even at 200 °C. However for a desorption pressure of 1 bar a temperature of 300 °C is needed. Due to this high operation temperature, coarsening

effects may occur and diminish the favourable properties of the material.

Therefore a critical issue for technical applications is the thermal stability of the required properties. Cycling experiments of Dehouche et al. [6] show that after 1000 H-loading and unloading cycles of Mg at 300 °C the crystallites grow from initial 20 up to 80 nm in diameter.

In this work, investigations concerning the sorption properties of nanocrystalline MgH_2 with and without Nb_2O_5 catalyst after annealing experiments are presented.

2. Experimental details

The nanocrystalline composite was synthesized by milling pure elemental magnesium hydride (95% purity, 5% magnesium) and a mixture of the elemental magnesium hydride and 0.5 mol% of Nb_2O_5 (99.9% purity) powders. Milling was carried out in a Fritsch P5 planetary ball mill with a ball to powder weight ratio of 400/40 g. MgH_2 was milled up to 20 h at 230 rpm. To prepare the samples with catalyst the milled Mg was mixed with 0.5 mol% Nb_2O_5 and milled

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for another 100 h. All milling experiments, preparation and transfer for characterization have been done in a glove box under a continuously purified Ar atmosphere. To study the sorption properties the specimen holders were sealed inside the box and then attached to a volumetric Sievert's apparatus designed by Hydro Quebec/HERA Hydrogen Systems.

The hydrogen pressure for all absorption measurements at 300 °C was 5 bar. All desorption measurements have been performed in vacuum.

3. Results and discussion

Fig. 1 shows absorption curves for a sample of pure milled Mg without additional catalysts measured at 300 °C after annealing the sample at temperatures between 300 and 400 °C in steps of 10 °C. The annealing times amounted to 5 h. The first absorption curve of the as-milled sample without annealing treatment shows fastest kinetics. The absorption rate decreases with increasing annealing time and temperature. In particular the first two annealing steps at 300 and 310 °C cause a distinct deterioration of the sorption properties.

The curves obtained after annealing at 310 up to 370 °C are quite similar. Annealing at 380 °C and higher temperatures for 5 h leads again to a slight deterioration of the absorption kinetics and the absorbed amount of hydrogen within 1500 s. The absorption rate for the first 80% of absorbed hydrogen decreases from the initial value of 0.8 to 0.2 wt.%/min after annealing the sample at 400 °C. Desorption measurements show similar features, see Fig. 2. The desorption rate is decreasing with increasing number of annealing steps. Whereas the desorption rate of the as prepared powder at 300 °C is -0.07 wt.%/min, after annealing at 400 °C it amounts to -0.04 wt.%/min. The capacity seems to diminish upon annealing as well. Fig. 3 shows absorption curves for Mg powder with Nb₂O₅ additive after annealing

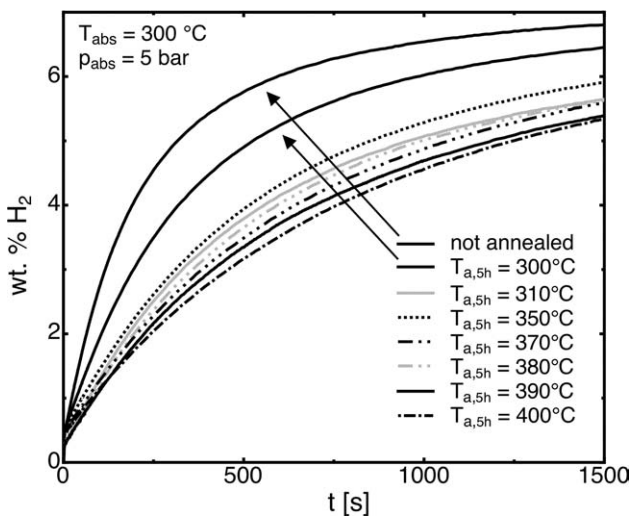


Fig. 1. Absorption kinetics of nanocrystalline MgH₂ at 300 °C after annealing treatments for 5 h each at the temperatures indicated.

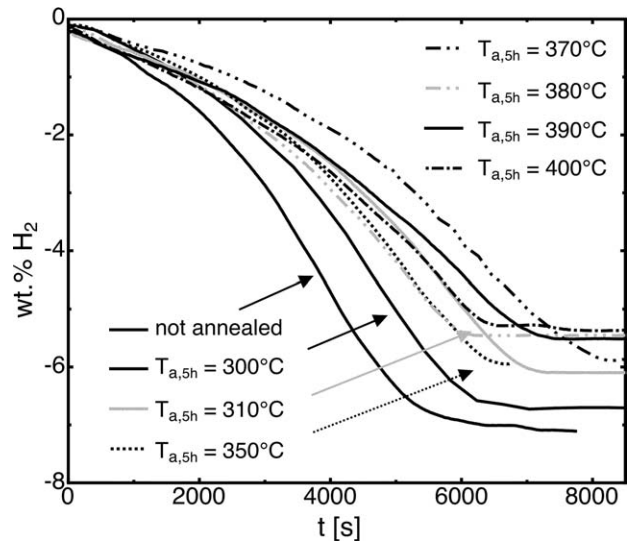


Fig. 2. Desorption kinetics of nanocrystalline MgH₂ at 300 °C after annealing treatments for 5 h each at the temperatures indicated.

treatments at different temperatures. In contrast to the material without catalyst, the kinetics seem to remain almost as fast as for the initial material up to the annealing temperature of 380 °C. The storage capacity decreases continuously with increasing temperature. Above 380 °C, a clear slow-down of the reaction kinetics is observed. Whereas the absorption rate of the as prepared sample is 3 wt.%/min, it reduces after the annealing at 390 °C to only 0.2 wt.%/min and after additional annealing at 400 °C further down to 0.05 wt.%/min. However, the curves belonging to the samples annealed at 390 and 400 °C level off at higher storage capacities than the one obtained at 380 °C. The respective desorption curves are given in Fig. 4. After annealing at 380 °C a clear slowdown in the desorption kinetics is found. The

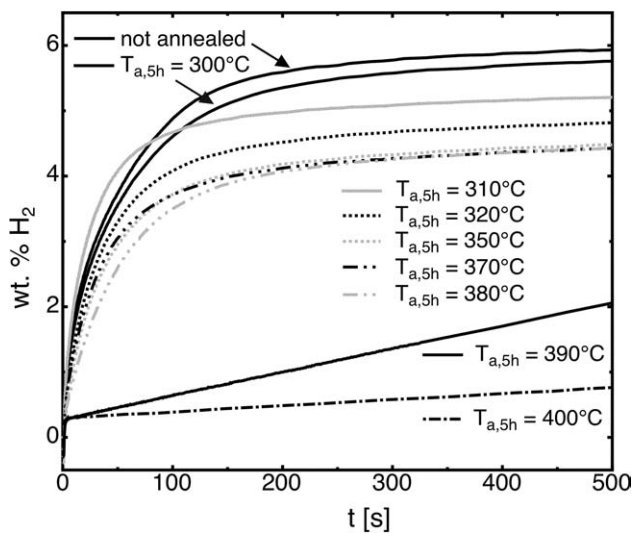


Fig. 3. Absorption kinetics of nanocrystalline MgH₂ with 0.5 mol% Nb₂O₅ at 300 °C after annealing treatments for 5 h each at the temperatures indicated.

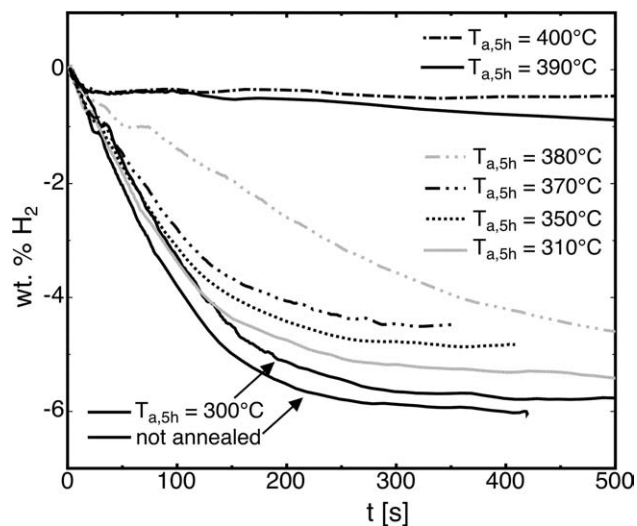


Fig. 4. Desorption kinetics of nanocrystalline MgH_2 at 300°C after annealing treatments for 5 h each at the temperatures indicated.

desorption rate for the first 80% of the stored hydrogen is decreasing from initially $-2.5 \text{ wt.}\%/\text{min}$ to $-0.7 \text{ wt.}\%/\text{min}$, $0.05 \text{ wt.}\%/\text{min}$ and $0.02 \text{ wt.}\%/\text{min}$ after additional annealing at 380 , 390 and 400°C , respectively. In order to clarify the issue of changing capacities, a long time measurement was performed after annealing for 5 h at 350°C (Fig. 5). After 3 h measuring time, the curve levels off at $6 \text{ wt.}\%$ compared to $7 \text{ wt.}\%$ for the as-milled material (Fig. 1). Interestingly, the absorption still continues at a much slower rate, and after another 1.5 weeks, the identical storage capacity is obtained. This demonstrates that the actual storage capacity does not change with increasing annealing temperature. However, the absorption process is divided into two distinct regimes. Within the first regime, the kinetics is as fast as in the initial state, while within the second regime, the kinetics is as

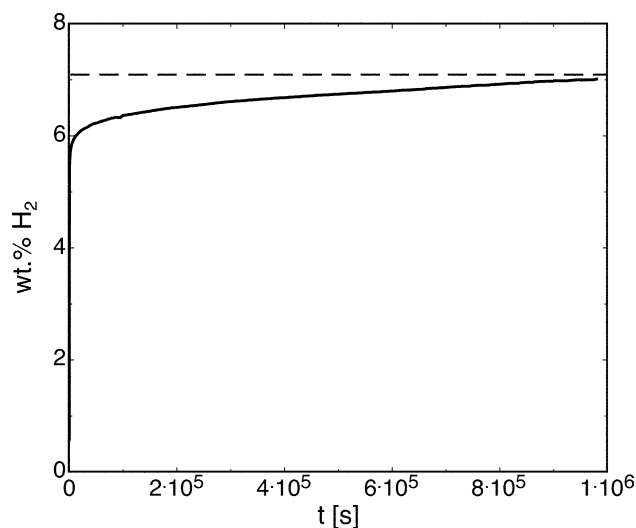


Fig. 5. Long-time measurement of absorption kinetics after annealing treatment for 5 h at 350°C . The curve for the as-milled MgH_2 material is added for comparison.

slow as in conventional, unmilled material. With increasing annealing time or temperature, the fraction of material converted within the second regime continuously increases at the expense of the fraction converted within the first regime.

According to Barkhordarian et al. [7] the rate-limiting step in the sorption properties of nanocrystalline Mg with low catalyst concentrations is the surface reaction. The changes at low temperatures in the sample without catalyst can be attributed to the relaxation and annealing of defects. Furthermore, the results point towards the special kinetic processes in nanocrystalline hydrogen storage materials concerning the enhanced hydrogen diffusion through grain boundaries. The changes at higher temperatures especially the division into two distinct regimes with different sorption kinetics can be attributed to grain growth processes. X-ray powder diffraction measurements of the samples used in this study show that the Mg grains are growing from an initial diameter of 11 to 200 nm after the annealing treatments of the sample at the different temperatures between 300 and 400°C . Crystallite boundaries are favorable nucleation sites for the phase transformation into the hydride and vice versa. Therefore, hydrides tend to form at the surfaces and interfaces first. Afterwards, the hydride has to grow, which means that hydrogen has to diffuse through the existing hydride layers into the crystallites and fill the volume. However, diffusion of hydrogen within the hydride phase is substantially slowed down as compared to the unhydrided phase, e.g. by a factor of 5000 for Mg. In conventional coarse-grained materials, the hydrides formed at the interfaces thus act as diffusion barriers towards the transport of hydrogen into the interior of the crystallites. Therefore, overall reaction kinetics of coarse-grained material is slow. In small-grained material, on the contrary, the volume of each crystallite is much smaller, and, thus, more easy to fill, because diffusion distances within crystallites are short. During annealing, the crystallites continuously grow and diffusion distances increase accordingly. Therefore, the fraction related to the first fast kinetics regime corresponds to the hydride formation along the grain boundaries, while the fraction related to the slow kinetics regime can be attributed to the bulk phase transformation, requiring diffusion through the existing hydride layer.

Furthermore, the comparison of the data with catalyst and without catalyst shows that there is a very clear deterioration of the sorption properties in case of the sample with Nb_2O_5 , at annealing temperatures above 380°C whereas there is only a slight deterioration in case of the sample without catalyst after annealing at the same temperatures. This indicates that the catalyst is stable up to temperatures below 380°C . After annealing at higher temperatures the sorption kinetics deteriorates drastically. After annealing at 400°C , the sorption kinetics of the sample with Nb_2O_5 is even worse than that one annealed at the same temperatures but without catalyst. Since MgO is more stable than Nb_2O_5 it can be concluded that at these temperatures Mg reduces the Nb_2O_5 catalyst, forming MgO, which further impedes hydrogen transport.

4. Conclusions

Nanocrystalline Mg with Nb₂O₅ catalyst shows a deterioration of sorption properties if annealed at temperatures higher than 300 °C. Grain growth leads to the formation of two distinct regimes with different sorption kinetics. The first regime is characterized by fast sorption kinetics, as found in nanostructured materials with catalyst. Within the second regime, the sorption kinetics slow down substantially to the kinetics of conventional coarse-grained material. Furthermore, the measurements show the existence of a temperature limit, above which the catalyst loses its functionality. For Nb₂O₅, this temperature limit amounts to 380 °C. This breakdown effect is attributed to the reduction reaction of the catalyst with Mg, forming Nb and MgO.

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