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Microstructure and hydrogen sorption kinetics of Mg nanopowders with catalyst

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Abstract

MgH_2 powders were ball-milled with and without catalysts (Nb_2O_5) under hydrogen in a high-energy mill for 10 h. Morphological, structural and microstructural characterization of the nanocomposites, including particle and crystallite size distribution were carried out before and after hydrogen absorption. In order to study the above-mentioned microstructural parameters imaging and X-ray scattering techniques (high-resolution X-ray diffractometry) have been employed. The effect of the particle and grain size on the hydriding/dehydriding kinetics of ball-milled MgH_2 + catalyst powders was analyzed. The grain and particle size reduction enhances substantially the hydriding/dehydriding.

Keywords: Magnesium; Nanocrystalline; Ball milling; Hydrogen sorption kinetics

1. Introduction

Magnesium hydride (MgH_2) is one of the most attractive hydrogen storage materials because of its high storage capacity (7.6 wt.%), light weight and low environmental impact [1], however, the hydrogen desorption reaction is too slow for practical use and requires high temperatures. By reducing the grain size of Mg/MgH_2 to nanocrystalline dimensions by ball milling (BM) and mechanical alloying (MA), the H-sorption kinetics are accelerated substantially [2,3]. It was demonstrated that when the grain size of Mg is reduced to the nanoscale range, the hydrogen desorption temperature (T_{des}) is decreased by about 100 °C [3,4]. Further significant improvement of the hydriding properties was performed by adding metal-oxides [3–6] as catalysts. It has been shown that the H-sorption of ball-milled nanocrystalline Mg/MgH_2 ($\sim$10 nm) with 0.2 mol% Nb_2O_5 as catalyst takes place completely for less than 10 min at 300 °C [4].

It is already proved that the grain size determines the favorable H-sorption kinetics, but for Mg/MgH_2, unlike Mg_2Ni, this is accomplished by a decrease in the H-capacity [7–9]. The influence of the particle size on the H-sorption kinetics is however still not sufficiently studied. In our recent study [6] it was proved that in addition to the grain size, the powder particle size reduction (to <1 μm region) improves the H-sorption kinetics of nanocrystalline Mg/MgH_2 powders. Mg/MgH_2 powders with the same grain size ($\geq$50 nm) and different particle size in the range 0.1–1 μm were investigated.

In the present work the microstructure and hydrogen sorption kinetics of nanostructured Mg powders with particles less that 1 μm, with and without catalyst (Nb_2O_5) were investigated.

2. Experimental

Pure commercial polycrystalline MgH_2 were ball-milled (BM) under hydrogen atmosphere of 5 atm for 10 h in a home made high-energy vibratory mill with 2 mol% Nb_2O_5 as catalyst (n-MgH_2-cat) and without catalyst (n-MgH_2). The applied milling time was sufficient in order to achieve a steady state microstructure.

The morphology of the powders was monitored by scanning electron microscopy (SEM) on a JEOL 5510 apparatus. The particle histograms were constructed by the use of an image processing software. The average pressure–composition isotherms (PCI) and H-sorption kinetics were measured by Sievert's-type apparatus at 573 K.

X-ray powder diffraction (XRD) using Cu Kα radiation was carried out on a Philips X'pert powder diffractometer in θ–2θ geometry. The microstructure was systematically studied by X-ray line profile analysis. Recently, a numerical model has been worked out using the convolutional multiple whole profile fitting procedure (CMWP). In this method the whole measured diffraction pattern is fitted by the sum of a polynomial background and physically well established theoretical profile functions corresponding to size and distortion. Therefore, the procedure provides a complete separation of size and strain contribution. The model assumes that the grains are spherical and have a lognormal size

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distribution:

$$G(L) = (2\pi)^{-1/2}\sigma^{-1}L^{-1}\exp\left[-\frac{(\ln(L/m))^2}{2\sigma^2}\right] \quad (1)$$

where L is the length variable, σ and m are the variance and median of the distribution, respectively. The fitting procedure provides several fitting parameters such as σ and m, volume averaged grain sizes:

$$\langle D\rangle = m\exp(2.5\sigma^2) \quad (2)$$

See elsewhere the detailed description of this analysis [10,11].

3. Results and discussion

Fig. 1(a) and (b) shows the XRD patterns of the n-MgH_2-cat and n-MgH_2 alloys, respectively. Broadened tetragonal β-MgH_2 peaks can be seen on both plots, indicating a drastic grain refinement due to the high-energy ball milling. The orthorhombic Nb_2O_5 peaks are sharper with relative high intensity. In the case of n-MgH_2-cat sample the peaks corresponding to the hydride and to the catalyst can be separated from each other, indicating that the mixing between the catalyst and hydride particles occurs on nanoscale, without any detectable reaction between the two constituents.

The normalized log-normal distribution function corresponding to the tetragonal MgH_2 phase of the n-MgH_2 powder obtained by the CMWP method is shown in Fig. 2(a). The calculated $\langle D\rangle$ values for the MgH_2 grains in the n-MgH_2 and n-MgH_2-cat alloys are 9 and 10 nm, respectively. As one can see these values lay on the decreasing tale of the distribution functions, since larger grains have larger contribution to the volume averaged grain size. BM with and without Nb_2O_5 for the same time has only a slight effect on the grain size of the MgH_2 powder. In a previous study we showed that this value is the lowest achievable volume averaged grain size, however, it can be attained after shorter milling times in the presence of Nb_2O_5 [8] therefore it can be declared that the main effect of the catalyst particles corresponds to the grain refinement rate.

As it can be seen on the SEM images with different magnifications in Fig. 3(a), the attrition process results in the formation of MgH_2 particles with sharp edges. Contrary, due to the presence of the rigid catalyst particles the MgH_2 agglomerates have smooth surface and spherical shape, see Fig. 3(b). After BM the MgH_2 powder, the average size of the powder particles decreases drastically from 40 to 50 μm [8] down to about 0.87 and 0.79 μm in n-MgH_2 and n-MgH_2-cat samples, respectively. The SEM imaging method provides similar values for the particle sizes, likewise to the volume averaged grain sizes obtained from diffraction technique.

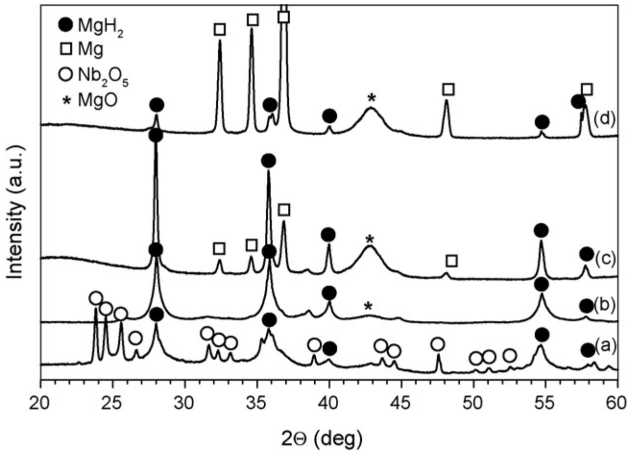

Fig. 1. XRD pattern of: (a) n-MgH_2-cat, (b) n-MgH_2, (c) n-MgH_2-abs and (d) n-MgH_2-des samples.

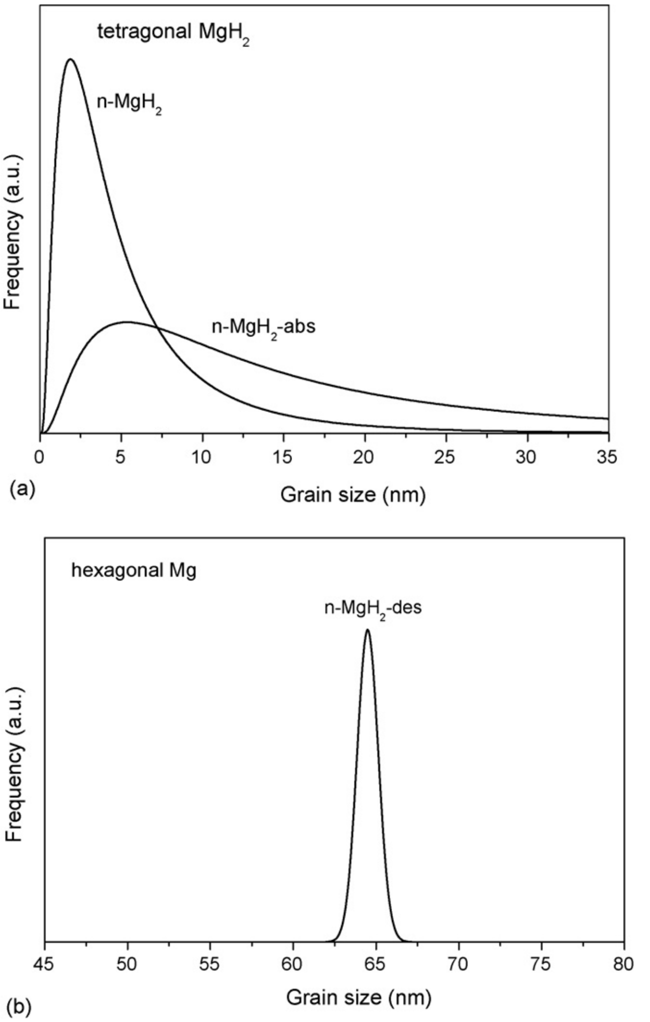

Fig. 2. Grain size distribution functions obtained from the CMWP method of: (a) tetragonal MgH_2 and (b) hexagonal Mg.

The desorption curves for n-MgH_2 and n-MgH_2-cat are practically identical as it can be seen in Fig. 4. The obtained maximum capacity for both sample is about 4.7 wt.%. The H-capacity is reduced mainly due to the particle and grain size refinement, however, it can also be decreased due to the Mg oxidation, see Fig. 1(c) and (d). In addition, accelerated surface oxidation of the powders with strongly reduced particle size (<1 μm) was detected by XRD. The absorption and desorption rate for n-MgH_2 was 1.1×10^{-2} and 1.4×10^{-2} wt.% s^{-1}, respectively, and are considerably higher than that of conventional polycrystalline Mg and nanocrystalline MgH_2 [3]. The n-MgH_2-cat sample exhibits an absorption rate of 1.0×10^{-2} wt.% s^{-1}, practically the same value as for the sample without catalyst,

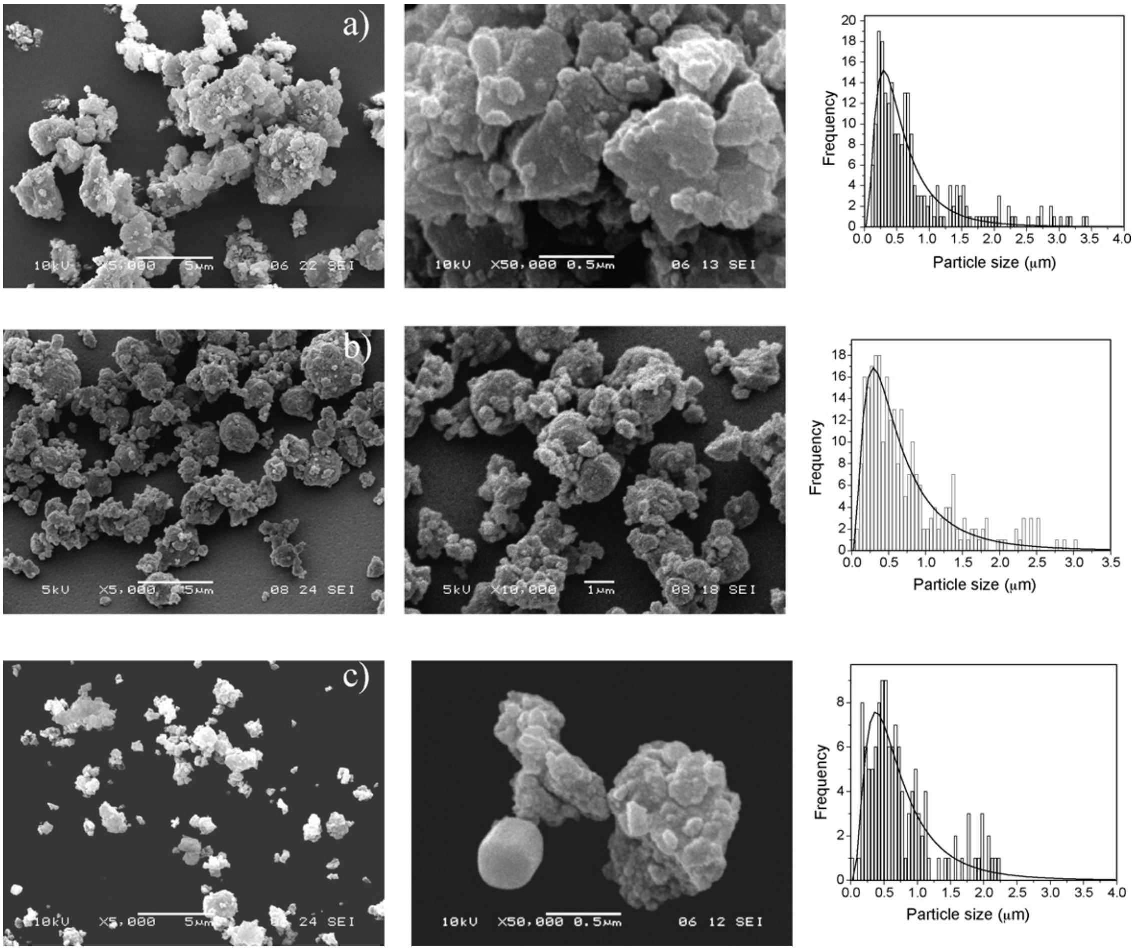

Fig. 3. SEM images and corresponding particle-size histograms of: (a) *n*-MgH_2, (b) *n*-MgH_2-cat and (c) *n*-MgH_2-abs samples.

demonstrating that in this system the Nb_2O_5 as catalyst has negligible effect on the kinetics. In our previous study hydrogen absorption rate of 2×10^{-2} wt.% s^{-1} was obtained for Mg–2 mol% Nb_2O_5 powder with extremely fine particles (100–500 nm) and average grain size larger than 50 nm [6].

In order to study the correlation of the microstructure on the hydriding/dehydriding process, the *n*-MgH_2 sample was exposed to several desorption/absorption cycles at 573 K as well. The XRD patterns of the absorbed (*n*-MgH_2-abs) and desorbed (*n*-MgH_2-des) states are shown in Fig. 1(c) and (d), respectively. After absorption some line sharpening occurs due to grain coarsening. In the case of *n*-MgH_2-des the main fraction of the powder transforms to hcp-Mg, although some residual MgH_2-peaks can still be seen, showing that the dehydriding process is not totally completed. The SEM images corresponding to the *n*-MgH_2-abs sample (Fig. 3(c)) present slightly finer particles of 0.78 μm average size, indicating only minor effect. On contrary, the grain size distribution function of the MgH_2 phase obtained from the CMWP method shifts to larger values and considerably broadens with a volume averaged grain size of 44 nm (see Fig. 2(a)). Interestingly, the Mg phase formed during desorption exhibits extremely narrow distribution with $\langle D \rangle = 65$ nm, see Fig. 2(b). It was found that during several cycles the microstructure of the powder alters between these two states. A high nucleation rate and a high density of randomly distributed pre-existing Mg nuclei can result in the observed sharp grain size distribution.

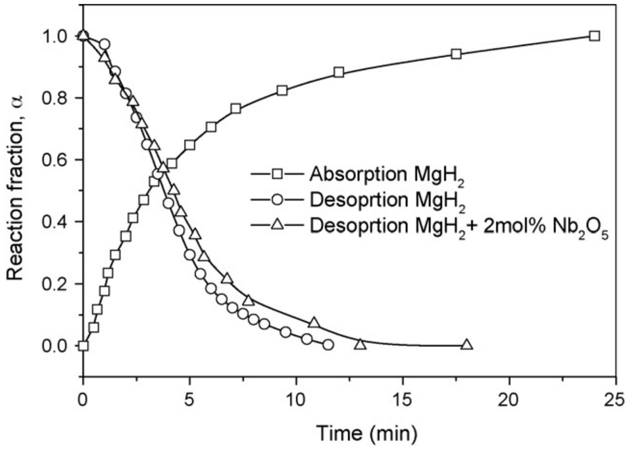

Fig. 4. Absorption and desorption curves of *n*-MgH_2-cat and *n*-MgH_2 obtained at 300 °C.

4. Conclusions

MgH_2 powders were ball-milled with and without catalysts (2 mol% Nb_2O_5) under hydrogen in a high-energy mill for 10 h.

The final volume averaged grain size was found to be about 10 nm in both cases and the size of the powder particles is also similar (≈0.80 μm). In parallel, the absorption rate for the *n*-MgH_2 and *n*-MgH_2-cat alloys is also identical, indicating that the catalyst particles do not have any direct influence on the microstructure, nanostructure and the sorption kinetics of the hydride.

The Mg phase formed during desorption exhibits extremely narrow grain size distribution with $\langle D\rangle = 65$ nm, while the MgH_2 phase after absorption shows a broad distribution with $\langle D\rangle = 44$ nm.

Acknowledgements

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