



Microstructural evolution of ball-milled MgH_2 during a complete dehydrogenation–hydrogenation cycle

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ABSTRACT

Repeated dehydriding–hydriding cycles of ball-milled nanocrystalline MgH_2 was carried out in a Sieverts'-type apparatus. In order to characterize the microstructural changes during a complete $\text{MgH}_2 \rightarrow \text{Mg} \rightarrow \text{MgH}_2$ transformation, the fourth desorption and subsequent absorption were interrupted at different hydrogenation stages. Convolutional multiple whole profile fitting procedure of the corresponding X-ray diffractograms was applied to reveal the evolution of microstructural parameters during the sorption cycle, such as average coherent domain size and crystallite size distribution. Complementary analysis of lattice parameters was also carried out. In this paper we demonstrate that analysing solely the evolution of microstructural parameters during cycling leads to similar rate-controlling mechanisms obtained by sorption kinetic measurements.

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1. Introduction

The novel approaches to reach hydrogen based energy systems resulted in a great interest to metal/intermetallic hydride storage solutions. Magnesium is considered as one of the most attractive hydrogen storage materials, mainly because of high storage capacity (7.6 wt.%), lightweight and low cost [1]. Nevertheless, high thermodynamic stability ($\Delta H = -75 \text{ kJ mol}^{-1}$) [2], high hydrogen desorption temperature (higher than 400°C) and relatively poor hydrogen absorption–desorption kinetics at temperatures below 350°C impedes the use of Mg in industrial applications.

It is well known that a breakthrough has been achieved in the magnesium hydride technology by preparing nanocrystalline hydride powders by using high-energy ball milling technique [3–7]. Ball milling of MgH_2 up to several hours results in fine nanopowder with a typical average grain size ranging from 10 to 30 nm [8–12], independently from the type of the milling apparatus and the milling conditions [13]. By reducing the grain size to nanocrystalline dimensions, the H-sorption kinetics are accelerated substantially, and the hydrogen desorption temperature is decreased by about 100°C [12,14,15]. In recent studies, it was demonstrated that the powder particle size reduction [16] as well as the shape of the particles [17] have also significant effect on the H-sorption kinetics of nanocrystalline Mg/MgH₂ powders.

Numerous studies have been presented on the hydriding–dehydriding reactions of powders in order to model their kinetic properties [18,19]. Calculations based on different rate-controlling mechanisms obtaining density of nucleation sites, H diffusion coefficient, shape of particles, predict the character of the desorption [20]. However, if a size distribution of the transforming grains is taken into account, the shape of the measured curves do not determine unambiguously the rate-controlling mechanism of hydrogen sorption, since the kinetics are strongly affected by the microstructure [21]. From the viewpoint of technological application, it is important to stabilize the kinetics and capacity during several cyclings, which are directly related to the microstructure of the hydriding powder. As reported in a recent paper, the first full dehydrogenation–hydrogenation cycle increase the average crystallite size of ball-milled MgH_2 from 9 to 18 nm and stabilize the microstructure, i.e. repeated cyclings do not have any further significant affect [22].

In the present study, the evolution of the microstructure of ball-milled MgH_2 during one full hydrogen desorption–absorption cycle will be monitored by applying X-ray line profile analysis.

2. Experimental

Commercial polycrystalline MgH_2 powder (supplied by Sigma-Aldrich, purity 99.9%, initial powder particle size $10 \mu\text{m}$ [12]) was ball-milled in a self-constructed Bakker-type vibratory mill [23] for 10 h under H-atmosphere of 6 atm in order to obtain nanocrystalline material. The milling vial as well as the ball (diameter

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60 mm) exhibiting vertical vibrations of 50 Hz were made of hardened stainless steel.

Hydrogen sorption kinetics were measured by a Sieverts'-type apparatus (PCT) at 573 K. The ~ 100 mg sample was loaded into a 10 cm^3 reactor. Desorption was measured in vacuum and absorption under hydrogen pressure of 8 bar. In order to achieve partially desorbed and absorbed states, the desorption (or absorption) process was interrupted in the PCT device at desired intermediate hydrogen content states by quenching the powder to room temperature.

The evolution of the microstructure during desorption-absorption cycles was monitored by X-ray powder diffraction (XRD) with Cu-K α radiation on a Philips X'pert powder diffractometer in θ - 2θ geometry and was characterized by X-ray line profile analysis. The instrumental pattern was measured on a NIST SRM660a LaB $_6$ peak profile standard material. The lattice parameters of Mg and MgH $_2$ were determined by a least square fitting algorithm considering the Bragg indices and the corresponding peak positions.

3. X-ray evaluation method

X-ray diffraction peak profile analysis is a powerful method for determining the microstructural properties of ultrafine-grained materials. The effects of crystallite size and lattice strain on peak broadening can be separated on the basis of their different diffraction order dependence. The standard methods of X-ray diffraction profile analysis based on the full width at half-maximum, the integral breadths and on the Fourier coefficients of the profiles provide the apparent crystallite size and the mean square of lattice strains [24–27]. Convolutional Multiple Whole Profile (CMWP) fitting procedure is well-established method for the determination of crystallite size distribution and the lattice defects of materials [28]. By using the appropriate instrumental diffraction pattern, the procedure can be used in a straightforward manner, either when the data are collected with monochromatic or with conventional K α doublet radiation. In this model it is assumed that the crystallites are spherical and have a lognormal size distribution:

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

where σ and m are the variance and median of the distribution, respectively. In the CMWP evaluation the whole measured diffraction pattern is fitted directly by the sum of background, theoretically constructed profile functions and measured instrumental profiles. These profile functions are calculated for each reflection

as the inverse Fourier transform of the product of the theoretically well-established size and strain Fourier coefficients and the Fourier coefficients of the corresponding measured instrumental profile:

(2) $A(L) = A_L^S(m, \sigma) A_L^D(\rho, R_e, \bar{C}, b) A_L^I$, where L is the Fourier length, A^S are the size Fourier coefficients, A^D are the strain Fourier coefficients and A^I are the Fourier coefficients of the measured instrumental profile. ρ (average volumetric defect density, mainly dislocations), R_e (effective outer cut-off radius of dislocations), \bar{C} (average dislocation contrast factor [29–30]) and b (Burgers vector) are the strain parameters. The size Fourier coefficients can be expressed as [31]:

$$A_L^S \cong \int_{|L|}^{\infty} (\mu^2 - |L|\mu) \operatorname{erfc}\left\{\left[\frac{\ln(\mu/m)}{2^{1/2}\sigma}\right]\right\} d\mu. \quad (3)$$

The background can be determined as a spline going through intensity values defined interactively by the user. The fitting procedure provides both the size and strain parameters, with m and σ the average coherent crystallite size

$$\langle D \rangle = m \exp(2.5 \sigma^2) \quad (4)$$

can be determined. The CMWP fitting program can be used via its web interface [32].

4. Results

As was demonstrated recently, the change in the sorption behaviour (i.e. rate and maximum capacity) of ball-milled MgH $_2$ is minor after a couple of hydriding cycles accompanied with constant microstructural parameters corresponding to each fully absorbed state [22], therefore the 4th complete cycle was selected to monitor the microstructural changes within one full desorption-absorption cycle. Fig. 1a and b presents the desorption and absorption curve during the 4th cycle, respectively, obtained by PCT. As seen, the desorption needs about 850 s for completion, while the absorption is completed within 750 s. The observed overall capacity (5.8 wt.%) is somewhat below the theoretical value [1], but comparable with literature data [14,33]. The partially desorbed states corresponding to 10%, 40% and 80% desorbed fraction are denoted by circles in Fig. 1. Since the fully desorbed powder containing only pure Mg is extremely flammable, the 80% fraction was not exceeded for safety reasons. Subsequent absorption was also stopped at different stages, i.e. 15%, 50% and 90% of Mg powder transformed to hydride. It is noted that each partial hydrogenation state was performed on a new dose of the ball-milled material.

A general view on the effect of hydrogen release and absorption during the investigated 4th complete cycle can be inferred

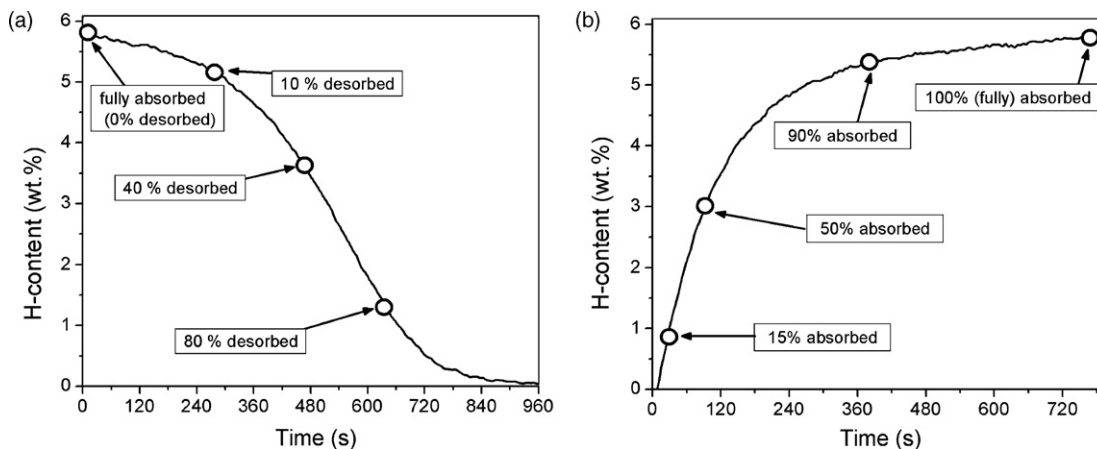


Fig. 1. Fourth desorption (a) and absorption curve (b) of ball-milled nanocrystalline MgH $_2$. Circles denote partially hydrided states.

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