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Synthesis of nanocrystalline MgH_2 powder by gas-phase condensation and in situ hydridation: TEM, XPS and XRD study

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Abstract

In this work, a two-step method for the preparation of nanocrystalline MgH_2 is presented, where the first step consists of synthesis of nanocrystalline Mg powder by the gas-phase condensation method (GPC) and the second of in situ hydridation leading to the formation of MgH_2 nanoparticles. By transmission electron microscopy (TEM) and electron diffraction (ED), crystalline Mg nanoparticles from GPC were found to have mean size within the range of 30–50 nm, while in the case of MgH_2 nanoparticles these values increase approximately 2–3 times mainly due to particles growth during the hydridation step. The X-ray diffraction (XRD) analysis shows the high conversion into the MgH_2 phase after hydridation. By X-ray photoelectron spectroscopy (XPS) metallic magnesium was detected below a magnesium oxide layer of 3–4 nm for the Mg sample prepared by GPC, which shows the efficiency of a novel sample transfer system without air exposure between N_2-glove-box, preparation chamber and experimental apparatus.

Keywords: Hydrogen storage materials; Nanostructured materials; X-ray diffraction; Photoelectron spectroscopies

1. Introduction

Much effort has been concentrated on studies of metal hydrides for hydrogen storage. Metallic magnesium and magnesium containing compounds are considered as promising candidates, since magnesium is an abundant, cheap and light metal with a high hydrogen sorption capacity of 7.6 wt.%. It has been shown that high energy ball milling of magnesium improves the hydrogen sorption properties [1–3], which presents a major drawback in its commercial application for hydrogen storage. In contrast to bulk magnesium, the one in the form of fine powder has many advantages: the powder has a large ratio of surface-to-volume which enhances availability of hydrogen on the metal surface, and nucleation of MgH_2 (which occurs on the surface) is remarkably increased. Also the growth of a compact hydride layer blocks further hydridation limiting the hydrogen storage capacity; this problem can be solved by decreasing the powder size [4].

Vapor condensation or sputtering techniques could be more effective than ball milling in developing nanocrystalline powders of very small particle size [5,6]. In these cases, each particle is produced on the nano-scale, but is not incorporated into larger configurations. It might be expected that they would have even better hydridation characteristics. Moreover, relatively long milling times are necessary to bring MgH_2 crystallites into nanometric regime, which often leads to incorporation of impurities from the ball-mill components.

In this work, we report the application of the gas-phase condensation method for developing nanocrystalline magnesium hydride powders to be used for hydrogen storage and transport purposes. The microstructural characterization of the samples allows us to evaluate parameters like size distribution and oxidation behavior that would influence the potential application of the materials for the hydrogen storage.

2. Experimental

2.1. Gas-phase condensation and in situ hydridation

The procedure consists of two main steps: synthesis of Mg nanoparticles, using the gas-phase condensation method already described in [5–8] followed by a hydridation leading to the formation of MgH_2 particles. Fig. 1 shows the experimental set up used for the Mg hydride nanoparticle production. The whole chamber consists of three main units: transfer unit (parts 1–3), evaporation unit (parts 4–10) and vacuum components (parts 11–14). The main synthesis takes place in the evaporation unit while the transfer one is used for sample transport without air exposure. The vacuum components ensure appropriate vacuum

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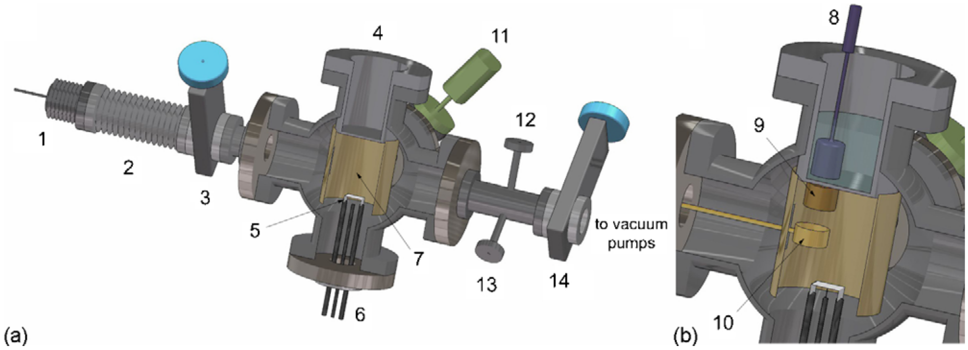

Fig. 1. (a) Experimental set up for the Mg hydride nanoparticles production by GPC method with (b) zoom on evaporation unit: (1) manipulator, (2) bellow, (3) UHV valve, (4) cooling/heating container, (5) evaporation boat, (6) electrical feedthrough with thermocouple, (7) Cu cylinder, (8) magnet in liquid nitrogen (scraping mode), (9) scraper with powder container, (10) scraper holder, (11) pressure sensor, (12) He inlet, (13) H_2 inlet and (14) UHV valve.

and/or gas dosage. First, the chamber is evacuated with a turbo-molecular pump to a residual pressure in the range of 10^{-7} Torr. The tantalum boat (part 5) with Mg turnings (Aldrich, 99.98% purity) is heated resistively up to a temperature chosen from the interval 1073–1273 K under atmosphere of 3 Torr of He. The evaporated Mg atoms condense in the form of ultrafine powder on a cold trap cooled by liquid nitrogen (part 4). After evacuation of the chamber and refilling with 2 bar of hydrogen, the powder is submitted to 25 h of thermal treatment at the temperature of 523 K. For this purpose the heating system is introduced into the cooling/heating container together with refractory sand, which allows an uniform heat distribution over the collected powder. Afterwards, the hydrogen is evacuated from the chamber and the obtained powder is stripped off by using a magnetic scraper (part 9) sustained by the action of a magnet situated outside the chamber.

2.2. Transfer without air exposure

The small container filled with hydrided nanocrystalline Mg powder is carefully placed into the scraper holder (part 10) connected to a manipulator (part 1) allocated in the transfer unit of the chamber. By stretching the flexible bellow (part 2) the scraper holder is introduced inside the unit. By closing the UHV valve (part 3) and dismounting the transfer unit, the sample is transferred to a glove-box. From the glove-box the sample could be transferred without air exposure to the TEM and XPS as described in [9].

2.3. Examination

TEM examination was carried out in a Phillips CM200 microscope working at 200 kV for Mg and MgH_2 powders. The crystal structure was studied by XRD analysis at an incidence angle of 1° using Cu Kα radiation in a Siemens D5000 diffractometer with a LiF (100)—monochromator for the diffracted beam in the detector arm. The XPS spectrometer used is a VG-Escalab 210 Spectrometer. It has a five channel hemispheric analyzer for electron registration, whereby the data acquisition takes place in constant energy analyzer mode with pass energy of $\Delta E = 30$ eV. The radiation used is the Al Kα from a non-monochromatized aluminium X-ray source with energy of 1486.6 eV.

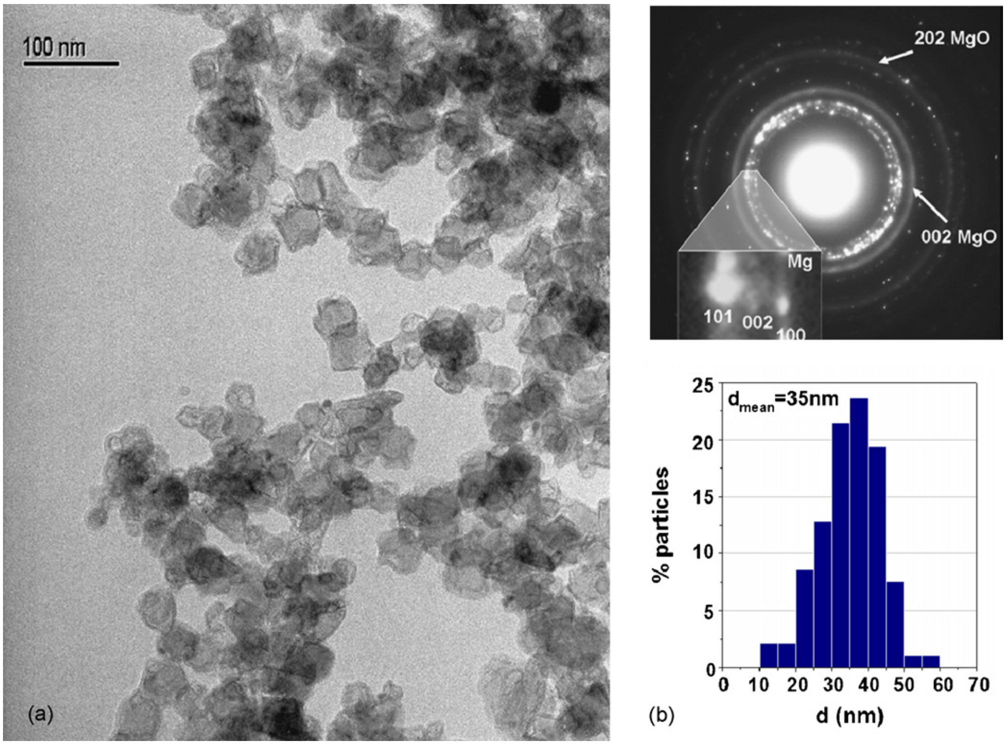

Fig. 2. (a) TEM micrograph and ED pattern (inset) of nanocrystalline Mg synthesized at 1073 K with (b) particle size distribution histogram.

3. Results and discussion

Fig. 2a shows the TEM micrograph and the ED pattern (inset) obtained for the Mg sample synthesized by GPC at 1073 K. The electron diffraction pattern taken for the same area shows a good crystallinity of the initial Mg sample and the diffraction rings are in agreement with typical d-spacings of Mg and MgO phases. The histogram of particle size distribution displayed in Fig. 2b illustrates that most of the particles are within the range of 30–50 nm with an average value of 35 nm. Particles do not form dense agglomerates and the narrow particle size distribution indicates a high size homogeneity of the sample.

Fig. 3a represents the TEM analysis of the nanocrystalline MgH_2 obtained by hydridation of the initial powder synthesized at 1073 K. In comparison to the initial Mg, the particles appear more heterogeneous, agglomerated and sintered among themselves. It means that during the hydridation particle growth and aggregation process take place leading to the formation of large areas of magnesium hydride. The particle size distribution (Fig. 3b) shows wider range approximately from 70 to 150 nm with average value of 109 nm. Nevertheless the particles prepared by the GPC method are less agglomerated and exhibit smaller particle size than those obtained by the ball-milling technique [10].

By XRD analysis of the hydrided powder (Fig. 4) the crystal phase can be identified as tetragonal magnesium hydride (β-MgH_2). All diffraction peaks are in agreement with this phase and no other peaks from metallic magnesium or magnesium oxides could be detected. A high conversion from magnesium to magnesium hydride is therefore concluded by the synthesis and hydridation procedure described in this work.

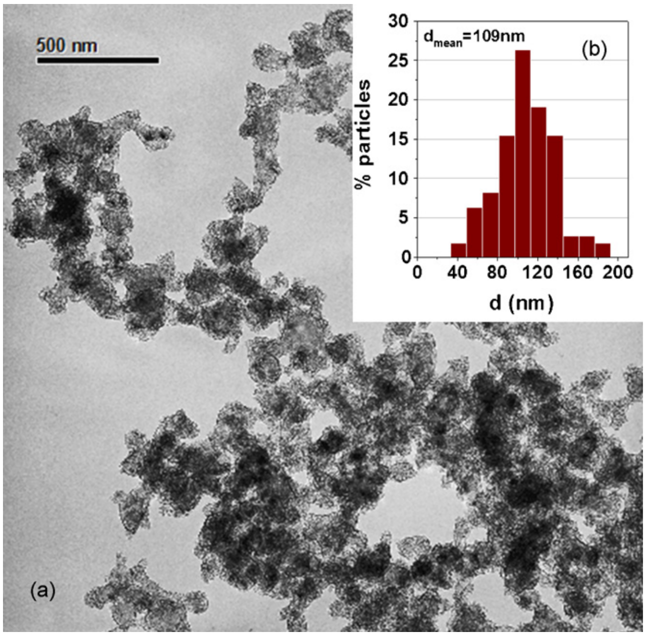

Fig. 3. (a) TEM micrograph of the nanocrystalline MgH_2 obtained by hydridation of the initial powder synthesized at 1073 K. (b) Particle size distribution of nanocrystalline MgH_2 powder.

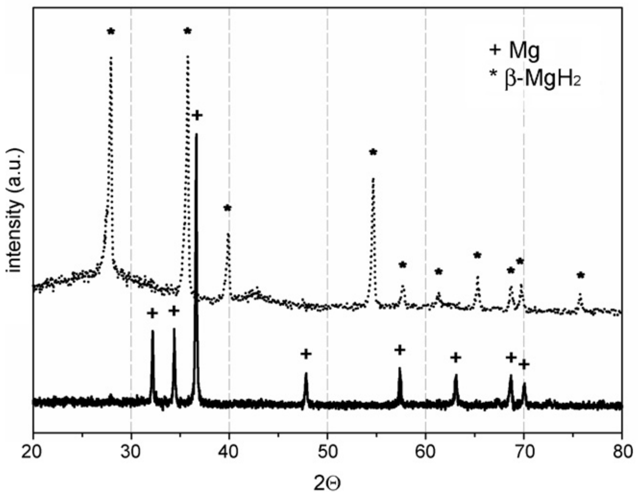

Fig. 4. XRD diffraction pattern of nanocrystalline Mg and MgH_2.

Fig. 5 displays the Mg2p and O1s photoelectron peaks and the Mg KLL Auger transition corresponding to the nanocrystalline Mg and MgH_2 samples. In the nanocrystalline magnesium, two components are clearly noticed at 49.6 and 51.2 eV corresponding to metallic and oxidized magnesium species, respectively. The O1s peak is composed of two peaks at ca. 531.4 and 533.2 eV attributed to oxide and hydroxide/water adsorbed on the surface of the magnesium particles, respectively. During hydridation the oxygen content of the MgH_2 powder is reduced as it is confirmed by calculating of the area ratio between the O1s peak from the MgH_2 and the Mg (0.8). This reduction is mainly due to the vanishing of the hydroxide component during the thermal treatment up to 523 K used during the hydridation step. The Mg2p after hydridation is very broad due to the overlapping of the different Mg compounds (oxide, hydroxide and hydride) whose differences in binding energy are too small to allow their identification [9]. In this sense, the analysis of Mg KLL Auger peak and the estimation of modified Auger parameter can provide further information for the characterization of the surface chemical state. The Mg KLL spectrum of the nanocrystalline Mg is char-

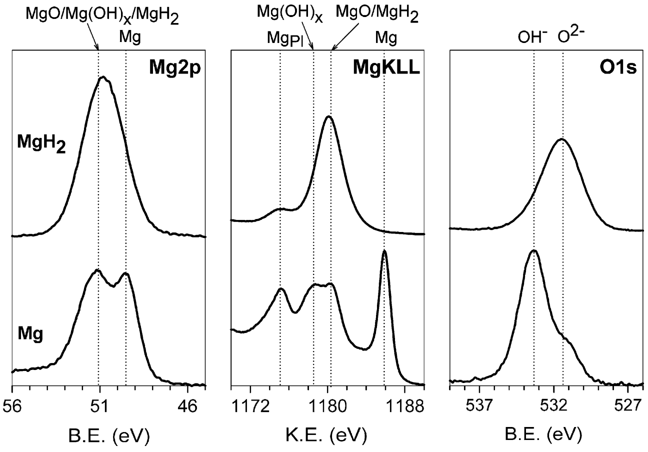

Fig. 5. XPS photoelectron (Mg2p, O1s) and Auger ($KL_{2,3}L_{2,3}$) peaks of nanocrystalline magnesium (Mg) and magnesium hydride (MgH_2) made by GPC.

acterized by the main transition at 1185.9 eV due to metallic magnesium although other features situated around 1180 eV are due to oxide/hydroxide species. After hydridation the spectrum changes noticeably and the main peak is shifted towards lower kinetic energies closer to the region where oxide and hydride phases are expected. The estimated Auger parameter for this sample, calculated by addition of the binding energy of the Mg2p photoelectron peak and the kinetic energy of the maximum of the Mg KLL Auger peak, is estimated to be 1230.9 eV which is in agreement with previously reported magnesium oxide species [9]. The thickness of this magnesium oxide surface layer was estimated to be 3–4 nm considering the attenuation of the XPS signal with the photoelectron path length also in accordance with a previous paper [9]. The degree of surface oxidation for the GPC samples is therefore similar to the one observed for nanocrystalline MgH_2 samples prepared by ball-milling procedures. The higher surface-to-bulk ratio of the GPC samples however lead to a higher total oxidation compared to the ball-milled powders.

4. Conclusions

In this work, a new methodology for the synthesis of nanocrystalline magnesium hydride particles based on the gas-phase condensation (GPC) technique is presented. The nanocrystalline MgH_2 phase is attained through in situ hydridation of Mg nanoparticles produced by the GPC technique. This method leads to small particles with particle sizes in the nanometric regime (∼100 nm) and low degree of agglomeration. The particles are composed of an inner core of crystalline β-MgH_2 surrounded by an oxidation layer of 3–4 nm, as determined by XPS. These morphological properties appear very advantageous for the improvement of the hydrogen sorption kinetics of these powders versus those yielded by conventional ball-milling techniques. However, the higher specific area makes them very sensitive to surface oxidation which can reduce the H_2-storage capacity.

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