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Using MgO to improve the (de)hydriding properties of magnesium

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Abstract

Of all the materials presently being investigated to safely store high volumes of hydrogen for mobile applications; magnesium remains the most attractive. Magnesium is a light, low cost metal with high capacity for hydrogen storage but its (de)hydriding kinetics have to be improved for practical applications. Recently, hydrogen kinetics in magnesium have been significantly improved by mechanically milling magnesium hydride with catalyst transition metals or metal oxides. Here, we report that similar improvements can be achieved without using a catalyst. Our results demonstrate that magnesium hydride milled with magnesium oxide exhibits dehydriding and hydriding kinetics as fast as those obtained with catalyst transition metals or metal oxides.

Keywords: A. Hydrides; A. Nanostructures; A. Oxides; C. X-ray diffraction; D. Catalytic properties

1. Introduction

Hydrogen storage in light materials could offer a safer and cheaper alternative to compressed or liquid hydrogen storage for vehicles application. Several materials have been considered to store hydrogen and at the moment magnesium is the only one that offers low cost and high storage capacity at the same time (7.6 wt%). Nevertheless, the practical use of magnesium for hydrogen storage is hindered by high Thermodynamic stability of its hydride and slow hydrogen kinetics [1–2]. There have been several attempts to overcome this problem. Hence, to improve the thermodynamic properties of magnesium, it was alloyed with Ni or intermetallic compounds such as $LaNi_5$, $FeTi_{1.2}$ and $ZrFe_{1.4}Cr_{0.6}$ [3–11]. On the other hand, to increase the reactivity of magnesium surface and improve hydrogen (de)hydriding kinetics (H-sorption), magnesium was alloyed with catalyst transition metals such as Ti, Fe, Co, Zr, Nb or Pd [12,13]. However, these attempts did not lead to a significant improvement of magnesium H-sorption properties for practical applications. Recently, it was found that the hydrogen absorption and desorption in magnesium could be improved by mechanically milling magnesium hydride (MgH_2) [14–17]. Further improvement was gained by milling MgH_2 with a 3d transition metal catalysts or metal oxides [18–22]. Huot et al. showed that milling MgH_2 with 5 wt% of Ti, V, Mn, Fe or Nb leads to a material that can desorb hydrogen within few minutes at 250 °C and absorb hydrogen at room temperature [23]. The transition metals used are believed to catalyse the desorption reaction of MgH_2 [24]. On the other hand, Barkhordarian et al. showed that milling MgH_2 with 1 mol% of TiO_2 V_2O_5, Mn_2O_3, Fe_3O_4 or Nb_2O_5

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leads to the same improvement of magnesium H-sorption properties [25]. The use of a cheap oxide compared to pure metal is of course an advantage from the perspective of application. The effect of the transition metal oxides on magnesium absorption and desorption kinetics is not clear. They are believed to enhance the dehydriding (hydriding) kinetics of magnesium by facilitating the recombination (dissociation) of hydrogen on the surface of magnesium particles. They may also help refining MgH_2 powder during mechanical milling and thus facilitate the formation of nanometric particles of MgH_2 with improved H-sorption kinetics [26,27].

In this work, we report that an important improvement of magnesium H-sorption properties can be achieved without using a catalyst. We have found that milling MgH_2 with MgO leads to a material with hydrogen kinetics as fast as those obtained with catalyst transition metals or their oxides. Since the improvement of magnesium H-sorption properties is a consequence of co-milling MgH_2 and MgO, we have characterised the effects of MgO on MgH_2 properties during the milling process. Milling two materials together is known to produce structural changes, alloying and particle size reduction [28–32]. Therefore, the evolution during milling of MgH_2 particles morphology, crystalline structure, thermodynamic and H-sorption properties has been analysed. Our results clearly demonstrate that co-milling MgH_2 and MgO does not modify MgH_2 structural or thermodynamic properties, but leads to an efficient decrease of its particle size and therefore improved H-kinetics.

2. Experimental

MgH_2 powder (95%, 20–60 μm) was purchased from Goldschmidt AG. MgO powder (99.99%, 0.5–30 μm) was purchased from Sigma–Aldrich.

MgH_2 was milled in a ceramic vial to reduce the problem of contamination from the milling tools, as we have found that lower contamination occurs in ceramic vials compared to stainless steel vials. MgH_2 was milled with or without 10 wt% of MgO in a Frischt P5 planetary mill in a glove box under Ar atmosphere. One hundred grams of zirconium oxide balls (Ø 10 mm, 3 g) were loaded in a 300 mL ceramic vial with 10 g of powder.

The structural characterisation of the samples was carried out with a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation. The diffraction patterns were analysed by the Rietveld method using the Fullprof software [33]. The following spatial groups have been used for the fit: *P4₂/mnm* for β-MgH_2 (rutile) tetragonal, *Pbcn* for γ-MgH_2 orthorhombic and *Fm3m* for MgO cubic. The fit of the diffraction patterns gave Rw_p values ranging from 10% to 12.%.

The sample morphology was characterised by SEM with a Zeiss DSM962 apparatus. Calorimetric measurements were performed with a DSC 404 C Pegasus from Netzsch. The measurements were carried out under a flow of high purity Ar (50 mL/min) with a heating rate of 5 K/min from 25 °C to 500 °C.

The hydrogen titration measurements were realised with a Sievert apparatus designed by HERA Hydrogen Storage Systems. The measurements were performed at 300 °C at 1 MPa of hydrogen for absorption and 0.1 kPa for desorption. High purity hydrogen was used (99.999%) and the weight of the sample was 100 mg.

3. Results

3.1. Morphological analysis

Fig. 1 shows the morphology of MgH_2 particles at two different milling times. MgH_2 particles with an average initial size of 40 ± 20 μm are broken into smaller ones throughout the milling (Fig. 1(a and b)). After 20 h of milling, large and small particles of MgH_2 can be observed and further milling leads to a higher reduction of MgH_2 particle size. As shown in Fig. 2, the size of MgH_2 particles rapidly decreases during the first 20 h of milling and finally reaches an average particle size of 1.00 ± 0.5 μm after 100 h of milling.

When MgH_2 is milled with MgO, the same reduction process of MgH_2 particle size takes place and MgO particles are also broken (Fig. 1(c and d)). After 20 h of milling, a large amount of small particles has been already produced. By continuing the milling, the size of MgH_2 particles further decreases. As shown in Fig. 2, when MgH_2 is milled with MgO the process of MgH_2 particle size reduction is accelerated. After 20 h of milling the average particle size is already 0.95 ± 0.5 μm, which corresponds to the particle size of pure MgH_2 milled for 200 h. The average particle size of MgH_2 milled with MgO stabilises after 100 h of milling to 0.44 ± 0.3 μm. Therefore, MgO facilitates the formation of smaller particles of MgH_2 in a shorter time.