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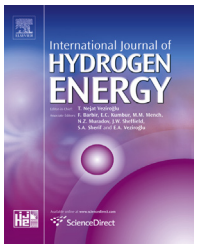

Nano-confined magnesium for hydrogen storage from reactive milling with anthracite carbon as milling aid

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ABSTRACT

The structure and properties of magnesium nanoparticles for hydrogen storage from reactive milling under hydrogen atmosphere with the carbon from anthracite coal carbonization as milling aid were investigated. Experiment showed that after 3 h of milling under 1 MPa of hydrogen with 30 wt.% of carbon additive, the magnesium particles were milled to 20–60 nm and hydrided into β-MgH_2 with a crystallite size of 29.7 nm. For the hydrogen desorption of the material, the onset temperature was determined to be 270 °C. In 270–390 °C, the enthalpy and entropy changes were calculated to be 44.5 kJ/mol and 83.8 J/(mol K), respectively, and the activation energy as pseudo first-order reaction was 127.1 kJ/mol. The carbon still played a role of nano-confinement for magnesium to prevent particles from coalescing in the process of repeatedly heating for hydrogen storage.

Introduction

Magnesium is a promising candidate for hydrogen storage in transport vehicles by its high reversible hydrogen capacity and abundant resource. Upon hydrogen absorption, the hydrogen first dissolves into magnesium crystal lattice to form solid solution, designated as α-MgH_2, in which the magnesium atoms are in hexagonal close packing (hcp) and the hydrogen content is rather low. Further hydrogenation produces MgH_2 of tetrahedral crystal lattice, referring to as β-MgH_2. The enthalpy and entropy changes of β-MgH_2 dehydriding reaction are 74.6 kJ/mol and 130 J/(mol K), respectively [1]. The onset and peak temperatures of hydrogen desorption are 290 °C and 420 °C, respectively, and its activation energy is as high as 156 kJ/mol [2]. Consequently, its application for hydrogen storage is limited by the high thermodynamic stability and poor reaction kinetics. Besides α and β phases, the MgH_2 of orthorhombic crystal lattice, referring to as γ-MgH_2, appears during ball milling [3–6], as well as under high compressive stress [7]. The γ phase is less stable than β phase, which is in favor of hydrogen desorption.

By reducing particle size, not only can the kinetics be improved, but also the thermodynamic stability can be decreased. Wagemans et al. [8] systematically investigated the effect of particle size on the thermodynamic stability of MgH_2

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using ab initio Hartree–Fock and density functional theory calculations, and the calculation demonstrated that the enthalpy change decreases significantly when the particle size decreases to nanoscale. For instance, a desorption temperature of 200 °C would be reached with an enthalpy change of 63 kJ/mol for β-MgH_2 of cluster size 0.9 nm. The magnesium at nanoscale provides a way to reduce the thermodynamic stability of MgH_2 as well as to improve the kinetics [9–13].

Nanoscale magnesium was synthesized by vapor deposition [14], electrochemical deposition [15], melt infiltration [16], etc. However, the percentage of magnesium in the samples prepared by these synthesis methods is rather low and the sample amount is also quite limited, which is far from application in transport vehicles. Mechanical milling is usually employed to decrease particle size. The cold welding of particles during milling hinders further decrease in particle size. Therefore, dispersion agents have been introduced into the milling process. Imamura et al. [17] investigated liquid milling aid, e.g. cyclohexane and benzene. Some researchers investigated using carbon as solid milling aid, e.g. graphite [18–20], carbon nanotubes [21], carbon black [22], and coal [23].

In this work, the carbon from anthracite coal by carbonization was used as milling aid for the preparation of MgH_2 by reactive milling under hydrogen atmosphere. It aims to investigate the effect of nano-confinement on the thermodynamics and kinetics of MgH_2 dehydriding.

Experimental

Raw materials

The hydrogen used as mechanical milling atmosphere has a purity of >99.99 vol.% (Qingdao Hengyuan Gas Company, China). The magnesium used for the preparation of hydrogen storage materials has a purity of >99.5 wt.% and a particle size of <0.074 mm (Tianjin Ruijinte Chemical Company, China).

The anthracite used as the precursor of carbon for milling aid is from Rujigou Mine, China. The coal has low ash content (2.44 wt.%, dry basis), low volatile matter content (6.76 wt.%), and high fixed carbon content (90.80 wt.%). The coal was firstly demineralized by alkaline melting and acid rinsing treatment to remove most of the mineral matter inherent to the coal, and the ash content was decreased to 0.05 wt.%. The KOH and NaOH used for coal demineralization have purities of >90 wt.% and >98 wt.%, respectively, and the hydrochloric acid used is analytical reagent of 36–38 wt.% of HCl (Tianjin Dalu Chemical Regent Company, China). Then, the coal was carbonized at 1500 °C for 1 h in an electric resistance furnace (SX2-1216 model, Shanghai Yuejin Medical Equipment Company, China), and thus the carbon was prepared.

Preparation of hydrogen storage materials

Ball milling to prepare hydrogen storage materials was carried out on a planetary ball-mill (ND7 model, Nanda Tianzun Instrument Company, China) with four stainless steel vials of 250 mL. The work revolution of the main axis of the mill was set at 270 r/min. Each vial was charged with 10 g of magnesium and carbon in a weight ratio of 70:30. Then the vials were purged with hydrogen and charged with 1 MPa of hydrogen. The milling time was normally set at 3 h except for research on the effect of milling time. During milling, the vials were recharged with hydrogen every other 0.5 h to maintain the hydrogen pressure at about 1 MPa. After milling, the materials were displaced in a glove box (NDZKS-1 model, Nanda Tianzun Instrument Company, China) with argon atmosphere to prevent the materials from being oxidized.

Characterization of the materials

The morphology observation of the materials was performed on a scanning electron microscope (SEM) of Hitachi S-570 operating at 25 kV and a transmission electron microscope (TEM) of Hitachi H-800 operating at 150 kV. The crystal

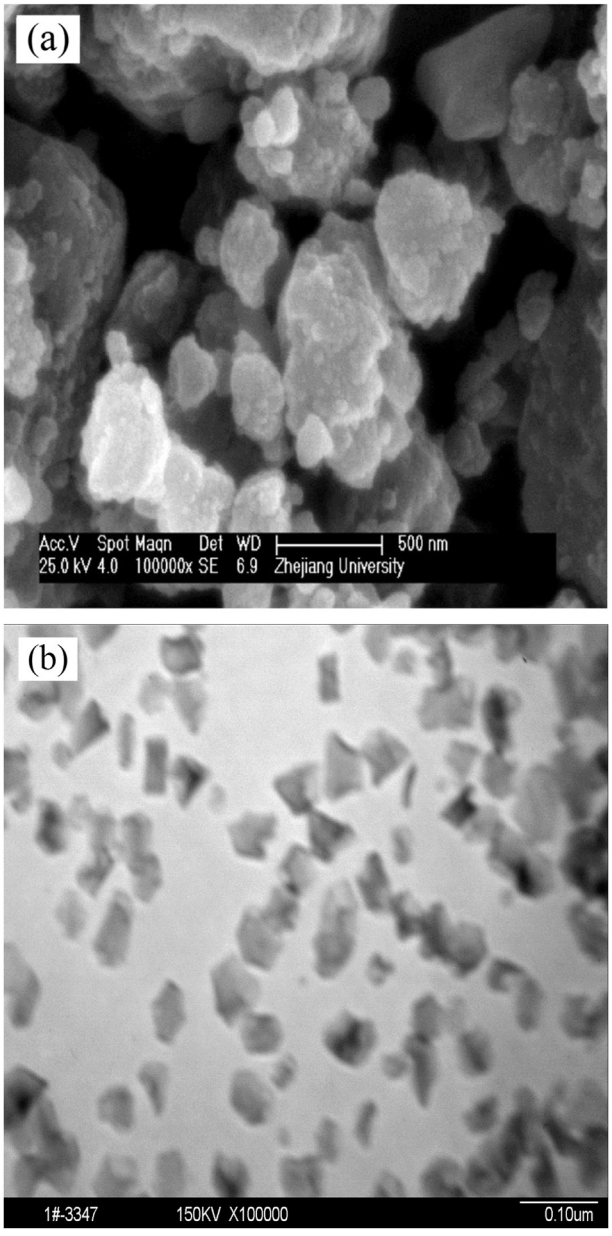

Fig. 1 – SEM (a) and TEM (b) images of the material from Mg and C in 70:30 milled under 1 MPa H_2 for 3 h.