



Effectiveness of crystallitic carbon from coal as milling aid and for hydrogen storage during milling with magnesium

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HIGHLIGHTS

- ▶ Carbon from coal acted as dispersant, lubricant and milling media for Mg milling.
- ▶ The Mg easily hydrided into β -MgH₂ and γ -MgH₂ during milling under hydrogen.
- ▶ Nanocomposites with hydrogen capacity of 6.67 wt.% were prepared by 3 h of milling.
- ▶ C–H dangling bonds made some contribution to hydrogen capacity of the composites.

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ABSTRACT

This paper is concerned with the functions of crystallitic carbon, prepared from anthracite coal by demineralization and carbonization, for making Mg-based nanocomposites for hydrogen storage by reactive milling under hydrogen atmosphere. The TEM and XRD analysis show that in the presence of 30 wt.% of crystallitic carbon, the Mg easily hydrided into β -MgH₂ of particle size 20–60 nm and crystal grain size 29.7 nm and a small amount of γ -MgH₂ after 3 h of milling under 1 MPa H₂. The hydrogen content of the composites is up to 5.81 wt.% determined by water displacement method, and its dehydrogenation peak temperature is 344.2 °C by DSC analysis. The enthalpy and entropy changes of the hydrogen desorption reaction are 42.7 kJ/mol and 80.7 J/mol K, respectively, calculated by the van't Hoff equation from the *p*–*C*–*T* data in 300–380 °C. With the extension of milling time, more γ -MgH₂ yielded, and the endothermic peak of γ -MgH₂ separated from that of β -MgH₂. The C–H dangling bonds in the hydrogenated carbon were determined by FT-IR analysis. The dehydrogenation temperature of the materials decreased with the addition of Co, Ni, Fe and Al.

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1. Introduction

Hydrogen is increasingly considered as an ideal fuel for the future because of its lightweight, zero pollutant emission, high conversion efficiency and potentially abundant production from renewable resources. It is proposed to use hydrogen in power transport vehicles as fuel for proton exchange membrane fuel cells (PEMFCs) or for internal combustion engines. Finding an effective method to store hydrogen is one of the critical steps required for hydrogen energy. Some efforts have been directed towards storing hydrogen in solids such as metal hydrides, complex aluminum hydrides, amides, borohydrides, nanostructure carbons, and metal organic frameworks (MOFs). Magnesium is a promising candidate for hydrogen storage because its theoretical hydrogen capacity is up to

7.6 wt.% and its resource abundance in the earth's crust is as high as 2.3 wt.%. However, its application is limited by the high temperature and low rate of hydriding and dehydriding [1,2]. The thermodynamic stability of magnesium hydride is too high, whose enthalpy change of hydrogen desorption reaction is as high as 74.6 kJ/mol [3].

Wagemans et al. systematically investigated the effect of crystal grain size on the thermodynamic stability of magnesium hydride using ab initio Hartree–Fock and density functional theory calculations [4], and the calculation demonstrated that the enthalpy changes of magnesium hydriding and dehydriding decrease significantly when the crystal grain size of magnesium decreases to nanoscale. The magnesium at nanoscale provides a way to reduce the thermodynamic stability of magnesium hydride as well as to improve the dehydriding kinetics to overcome the application barrier. Therefore, it is important to lower the size of magnesium particles. However, synthesis of magnesium nanoparticles less than

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100 nm is very difficult because of the high reactivity and cold welding property of magnesium nanoparticles.

Zhang et al. synthesized magnesium nanoparticles around 40 nm by acetylene plasma metal reaction [5]. Aguey-Zinsou et al. prepared magnesium nanoparticles of 5 nm by electrochemical synthesis [6]. de Jong et al. prepared 3D carbon-supported magnesium crystallites less than 5 nm using infiltration of nanoporous carbon with molten magnesium [7]. However, using the above synthesis methods, the percentage of magnesium in the prepared samples was rather low and the sample amount was also quite limited, which was far from application.

Ball milling has been employed to decrease the particle size of magnesium. However, it is difficult to obtain magnesium with particle size less than 500 nm by milling because agglomerating and welding of powder during milling process hinder further decrease in particle size. Dispersion agents have been introduced into the milling process to prevent magnesium particles from agglomerating and welding. Imamura et al. investigated liquid milling aid, such as cyclohexane and benzene [8,9]. Some researchers investigated using carbon as solid milling aid, such as graphite [10–12], carbon nanotubes [13,14], carbon black [15,16], and coal [17]. Anyway, dispersive nanoparticles have been prepared with the help of milling aids although the milling time was as long as tens of hours even 200 h.

The hydriding and dehydriding kinetics of magnesium can be significantly improved by the use of catalysts, such as Ni [18], Cu [19], Co [20], Fe [21], Ti [22], Mn, Al [23], Cr₂O₃ [24], Fe₂O₃ [25], WO₃ [26], Nb₂O₅ [27], and TiF₃ [28]. The hard particles of catalysts also play a role of milling media during the milling process. The improvement of kinetics is attributed to the decrease of magnesium particle size and the catalysis of the catalysts.

Besides as fuel, hydrogen is widely used as reactant in the process of hydrogenation, such as hydrocracking, hydrodesulfurization and hydrodenitrogenation. The H–H bond energy of hydrogen is as high as 436 kJ/mol, and consequently it is necessary to introduce catalyst and high pressure hydrogen into the hydrogenation reaction system. The hydrogen with lower dissociation energy in the hydrogen storage materials is easier to react with the bonds of hydrocarbons than molecular hydrogen. The stability and diffusion kinetics of atomic hydrogen in hydrogen storage materials should be consistent with the activation temperature and reaction kinetics of hydrocarbons. It means that the requirement is different from the materials to provide hydrogen for fuel cells, especially to the dehydrogenation temperature which may be not confined to be as low as less than 150 °C. To prepare hydrogen storage materials of specific dehydrogenation characteristics for industrial hydrogenation process to reduce the harsh requirements for catalyst and hydrogen pressure is still a challenge [29].

In this work, crystallitic carbon, prepared from anthracite coal by demineralization and carbonization, was used as an additive into magnesium to prepare nanocomposite material for hydrogen storage by reactive milling only for 3 h under 1 MPa of hydrogen, and catalytic metal Co, Ni, Fe and Al were introduced to adjust the dehydrogenation properties of the materials.

2. Experimental

2.1. Raw materials

The hydrogen used as ball-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), and the catalytic metal Co, Ni, Fe and Al used all have a purity of >99.0 wt.% and a particle size of

<0.15 mm (Shanghai Aibi Chemical Reagent Company, China). The anthracite coal used as the precursor of crystallitic carbon is from Rujigou Mine, China. The coal has low volatile matter content (6.60 wt.%, dry basis), low ash content (8.55 wt.%), and high fixed carbon content (83.00 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.% (Tianjin Dalu Chemical Reagent Company, China).

2.2. Preparation of crystallitic carbon

The anthracite coal was 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.% before carbonization to prepare crystallitic carbon. In the process of demineralization, the raw coal was smashed and ground to less than 0.074 mm, and then mixed with alkali (mixture of equal weight of KOH and NaOH) in a weight ratio of 5:1 in a stainless steel vessel which was treated via passivation, and heated at 400 °C for 1.5 h, and then rinsed with deionized water until the rinse water became neutral. Next, it was soaked in hydrochloric acid of 4 wt.% in a ratio of 1 g to 200 mL, and heated at 80 °C for 4 h in a thermostatic water bath, and then rinsed with deionized water until the rinse water became neutral. After demineralization, the coal was enclosed into a crucible, and carbonized at 1500 °C for 1 h in an electric resistance furnace (SX2-1216 model, Shanghai Yuejin Medical Equipment Company, China) with argon flow to protect the sample from being oxidized, and finally the crystallitic carbon of microcrystalline graphite structure was obtained.

2.3. Preparation of hydrogen storage materials

Ball milling to prepare hydrogen storage materials was carried out on a planetary ball-mill (ND7-2 model, Nanda Tianzun Instrument Company, China) with four stainless steel vessels of 500 mL. The milling media were stainless steel balls composed of 3000, 800, 100 and 5 balls of diameter 3, 6, 10 and 20 mm, respectively. The work revolution of the main axis of the mill was set at 180 r/min. Each vessel was charged with 30 g of start materials, and the weight ratio of ball to start materials was about 30:1. Then the vessels were purged with hydrogen, and charged with 1 MPa of hydrogen. The milling time was normally set at 3 h except for the research on the effect of milling time. During milling, the vessels were recharged with hydrogen every other 0.5 h in order to maintain the hydrogen pressure at about 1 MPa. After milled, the materials were displaced in a glove box (NDZKS-1 model, Nanda Tianzun Instrument Company, China) with argon atmosphere to prevent it from being oxidized.

2.4. Characterization of the materials

The morphology observation of the materials was performed on a Hitachi H-800 transmission electron microscope (TEM) operating at 150 kV. The high resolution transmission electron microscope (HRTEM) observation was carried out using a JEOL JEM-2100 electron microscope operating at 200 kV. The crystal structure of the materials was determined by a Rigaku D/Max-rB X-ray diffraction instrument (XRD) at a scanning speed of 2 deg/min and in steps of 0.02°. The functional groups of the materials were determined by a Nicolet 380 Fourier transform infrared spectroscopy (FT-IR) using cold-pressed KBr pellets. The thermoanalysis of the materials was carried out on a Netzsch STA 449C simultaneous DSC–TG thermoanalyzer at a heating rate of 10 °C/min and an argon flow rate of 80 mL/min. The pressure–concentration–temperature (*p–C–T*) curves (i.e. pressure–composition isotherms, PCIs) of the materials were measured on an apparatus deigned according to Sieverts

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