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The Effect of TTNT Nanotubes on Hydrogen Sorption using MgH_2

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Nanotubes are promising materials to be used with magnesium hydride, as catalysts, in order to enhance hydrogen sorption. A study was performed on the hydrogen absorption/desorption properties of MgH_2 with the addition of TTNT (TiTanate NanoTubes). The MgH_2-TTNT composite was prepared by ball milling and the influence of the TTNT amount (1.0 and 5.0 wt. (%)) on the hydrogen capacity was evaluated. The milling of pure MgH_2 was performed for 24 hours and afterwards the MgH_2-TTNT composite was milled for 20 minutes. Transmission Electronic Microscopy (TEM) and Scanning Electron Microscopy (SEM) were used to evaluate the nanotube synthesis and show the particle morphology of the MgH_2-TTNT composite, respectively. The Differential Scanning Calorimetry (DSC) examination provided some evidence with the shifting of the peaks obtained when the amount of TTNT is increased. The hydrogen absorption/desorption kinetics tests showed that the TTNT nanotubes can enhance hydrogen sorption effectively and the total hydrogen capacity obtained was 6.5 wt. (%).

Keywords: *hydrogen storage materials, magnesium hydride, mechanical milling, nanotubes*

1. Introduction

Mg is an abundant metal and has a high capacity to store hydrogen (~7.6 wt. (%)) and for these reasons it is very attractive to be used in hydrogen storage. However, there are limitations in practical applications due to the low absorption/desorption kinetics and high service temperature. The development of a nanocatalyst that combined with magnesium hydride can help to overcome such limitations is much studied nowadays. Nanotubes have been studied[1,2] for the past decade and showed to be effective catalysts for hydrogen storage using magnesium[3-8]. However, most of the studies reveal the use of carbon-based nanotubes and not much has been investigated on the use of nanotube made from titanium oxide. The investigation of the hydrogen absorption/desorption properties of MgH_2 with the addition of TTNT (TiTanate NanoTubes) has been performed in the present work.

2. Experimental

The TTNT nanotubes were synthesized via alkaline hydrothermal route using commercial TiO_2 powder as a starting material dispersed in NaOH 10 M. The mixture was stirred for 24 hours at 120 °C and washed with water in order to remove the unreacted NaOH[9]. Transmission electron microscopy (TEM) images of the synthesized product were recorded by using a JEOL 2010 equipment. The MgH_2 powder supplied by Sigma-Aldrich was ball milled with tungsten carbide balls under H_2 atmosphere for 24 hours at 300 rpm using a Fritsch P-6 planetary mill. After that, the MgH_2 was milled for 20 minutes more with 1 and 5 wt. (%) of TTNT. The samples were handled in a glove box under argon atmosphere. The hydride phase stability was examined by using a differential scanning calorimeter (DSC- Setaram) under argon atmosphere. The kinetics tests were performed by an automatic Sievert's type apparatus designed by PCT-Pro 2000. The MgH_2-TTNT morphology was analyzed by using scanning electron microscopy (SEM – JEOL JSM 6460LV). The hydrogen absorption and desorption measurements were performed at 10 bar and 0.1 bar of hydrogen pressure, respectively, at 350 °C.

3. Results and Discussion

The TTNT sample showed extensive formation of nanotubes (Figure 1a). TTNT nanotubes were open-ended tubes as shown in Figure 1b with multiple 3-5 walls and diameter around 10 nm.

The SEM image on Figure 2a of the MgH_2 + 5 wt. (%) TTNT sample showed an agglomerate of small particles with size ranging from several nanometers to micrometers. Based on the EDS result, Ti is present in MgH_2 associated to the TTNT and the presence of Au is due to the coating performed during sample preparation (Figure 2b).

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Figure 3 shows the DSC curves for MgH_2 after being milled with TTNT catalyst and without the catalyst at a heating rate of 10 K/min. Endothermic peaks were observed for all samples. A peak at 665 K was obtained for the MgH_2 + 5 wt. (%) TTNT sample. A similar behavior was observed when the same amount of boron nitride nanotube was used[5]. During milling high-pressure metastable γ-MgH_2 (orthorhombic) was partially formed from β-MgH_2 phase. The γ-phase disappears in the first desorption and it is not formed again in the following hydrogenation cycle[10]. The DSC curve of MgH_2 + 1 wt. (%) TTNT sample shows two peaks which correspond to the decomposition of these two hydride phases at different temperatures (676 and 730 K). However, the MgH_2 + 5 wt. (%) TTNT sample showed only one peak related to hydrogen decomposition (665 K). Although the DSC curve of this sample showed only one peak, the two hydride phases (β-MgH_2 and γ-MgH_2) are also present in this sample but the hydride decomposition temperature of each phase are so close that occurs overlapping of these peaks.

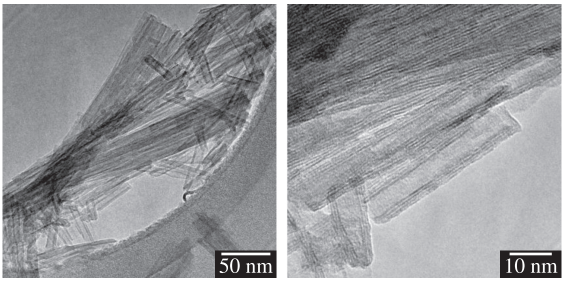
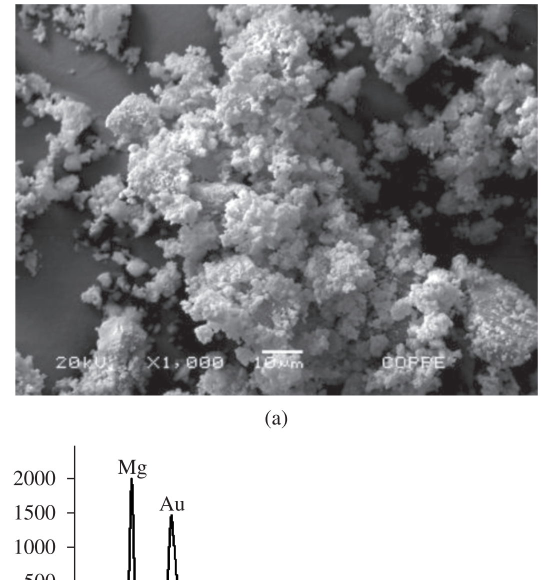


Figure 1. TEM image of a large group of aligned nanotubes in TTNT sample.



(a)

(b)

Figure 2. SEM image of MgH_2 + 5 wt. (%) TTNT sample (a) and elemental composition identified by EDS (b).

The hydrogen absorption/desorption kinetics of samples were investigated at 350 °C under an initial pressure of 10 bar for absorption and 0.1 bar for desorption (Figure 4a, b). The sample with a smaller amount of TTNT, MgH_2 + 1 wt. (%) TTNT, attained 5.2 wt. (%) of hydrogen in 5 minutes. The MgH_2 without catalyst sample attained almost the same capacity but only in 30 minutes at 350 °C (Figure 4a). This result suggests that the addition of TTNT enhanced the absorption kinetics. However, when more catalyst was added, the MgH_2 + 5 wt. (%) TTNT sample, the hydrogen capacity decreased to 4.5 wt. (%) of hydrogen in 5 minutes. The desorption results represented in Figure 4b show the same behavior verified in the absorption ones where the MgH_2 + 1 wt. (%) TTNT sample showed the highest hydrogen absorption capacity. However, the increase of the catalyst addition favored the hydrogen desorption kinetics and this result can be correlated to the DSC one since the hydrogen desorption occurs at a lower temperature for the sample containing more catalyst. The comparison between the results obtained for the MgH_2 milled without catalyst and the MgH_2 with addition of only 1 wt. (%) of TTNT, revealed an enhancement of the hydrogen absorption/desorption kinetics when the catalyst was added. This can be attributed to the fact that the hydrogen diffusion on nanotubes occurs preferably along the nanotube length than in the radial direction[1,11]. This is based on the fact that the hydrogen molecules penetration is more likely to occur on the channels along the tube than on the walls that are formed by a dense layer of TiO6 octhaedrons[1]. In the present work, only a small amount of the titante nanotube catalyst, 1 wt. (%), was required to obtain a high adsorption capacity value. For this reason the material could be used as a catalyst and is more effective when compared to the same amount of other catalyst, niobium oxide, used previously in the same conditions and that presented a capacity of only 1.7 wt. (%) in 5 minutes[12], in contrast to the value of 6.5 wt. (%) obtained here.

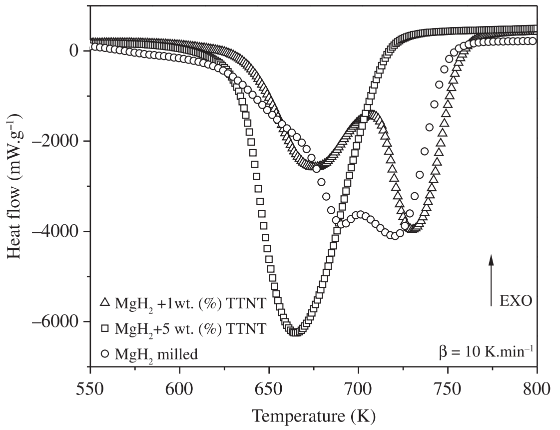
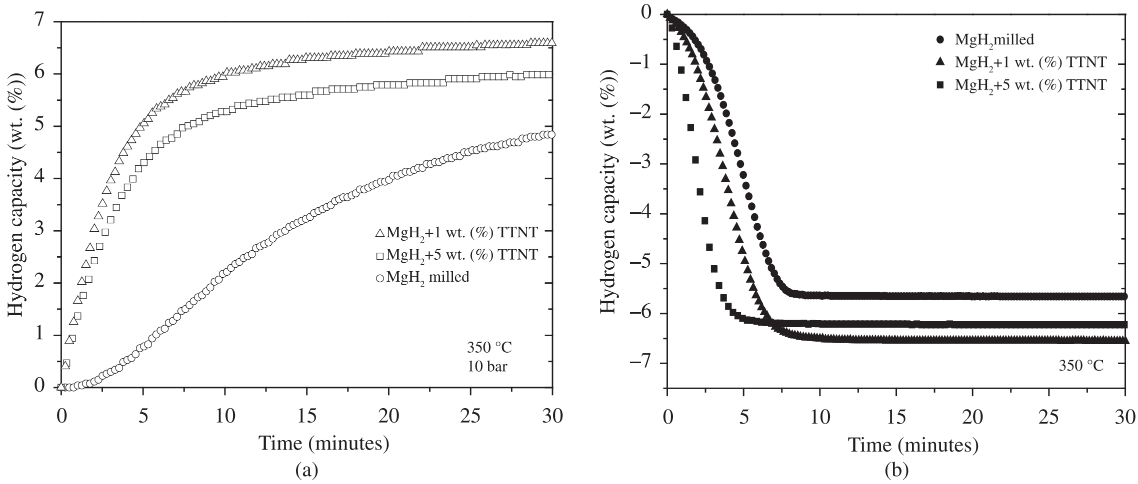


Figure 3. DSC curves of MgH_2 + 1 wt. (%) TTNT, MgH_2 + 5 wt. (%) TTNT and MgH_2 milled.



(a) (b)

Figure 4. Hydrogen absorption (a) and desorption curves (b) of MgH_2 + (1 and 5 wt. (%)) TTNT and MgH_2 milled without catalyst.

4. Conclusions

Titanate nanotubes (TTNT) synthesized using titanium oxide as precursor were used as catalysts to enhance hydrogen sorption. The kinetics tests were conducted with two amounts of TTNT (1 and 5 wt. (%)) at 350 °C. TTNT nanotubes showed to be a promising catalyst for this purpose since they improved the kinetics and hydrogen capacity when compared to the MgH_2 without catalyst from 5.5 wt. (%) to 6.5 wt. (%) when only 1 wt. (%) of TTNT is added, at 350 °C.

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