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Synthesis by High-Energy Ball Milling of MgH_2-TiFe Composites for Hydrogen Storage

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Abstract. The aim of this work is to investigate the influence of some processes variables on the microstructure and hydrogen absorption kinetics of MgH_2 - X wt.% TiFe composites. Samples were synthesized by high-energy ball milling in a planetary (X = 40, 50, 60) and shaker mill (X = 40) under high-purity argon atmosphere. Commercial MgH_2 instead of Mg powder was used in order to reduce adherence on the vial and balls. TiFe powder was previously produced by ball milling a mixture of TiH_2 and Fe powders followed by a reaction synthesis at 600ºC. Milled composites samples were characterized by XRD and SEM analysis. Milling time was preliminary investigated (X = 40) in the planetary ball mill (6 to 36h). TiFe particle size reduction was shown to be difficult since they are surrounded by MgH_2 matrix. Strong particle reduction was obtained by using a shaker mill only for 2 hours and adding cyclohexane as process control agent. No reaction between MgH_2 and TiFe compound was observed in any milled sample. Hydrogen absorption kinetics measurements of the as-milled samples were conducted on an Sieverts' type apparatus at room temperature after hydrogen desorption at 350ºC under vacuum. The best hydrogen kinetics (3 wt% at the first hour) was attained by the planetary milled sample (36 h). Higher hydrogen capacity was observed for the sample milled in the shaker mill (4.0 wt.%), but only after 13h.

Introduction

As a hydrogen storage material in the solid state, Magnesium has been attracted very much attention by several reasons: high hydrogen gravimetric (7.6 wt%) or volumetric (6.5 H atoms.cm^{-3}) capacity, combined with low density (1.45g.cm^{-3}) and cost (Magnesium is the eighth most abundant element in the earth's crust). Besides, magnesium hydride has the highest energy density (9 MJ/kg of Mg) among all reversible hydrides for hydrogen storage [1].

The development of hydrogen storage materials however is currently faced with problems that can be summarized in two: materials have either appropriated hydrogen absorption / desorption temperatures near room conditions, but low storage capacity, or high volumetric or gravimetric storage capacities, but very high desorption temperatures. The practical application of magnesium faces the second problem (the desorption temperature is in a range of 573 to 673 K) and relatively low kinetic of hydrogen absorption / desorption [2].

Lower desorption temperatures (< 300°C) has been reported for nanocrystalline MgH_2 obtained by high energy ball milling, severe plastic deformation techniques (like equal-channel angular pressing), and trough the addition of various catalysts [3]. Despite the advances made with such techniques, especially in improving the desorption kinetics, temperatures of hydrogen desorption

are considered still high, at least by the standards of the US DOE [4] wich established as the ultimate goal a temperature range for hydrogen release from 233 to 358 K.

Among several catalyst (for the hydriding of magnesium) or destabilizing (of the magnesium hydride) materials are the intermetallic compounds of transition metals. The strategy of using composites is, in this case, based on the mixture of dissimilar materials, seeking to take advantage of what is best in each component. In this case, it is intended to combine TiFe, which absorbs and desorbs hydrogen at or very near room temperature, with Mg, which has higher storage capacity.

High energy ball milling have been used to process such composite, starting normally from powder mixtures of Mg and TiFe alloy in various proportions [5-7]. In those works, besides stoichiometric TiFe compound, $Ti_{1.2}Fe$ [5] and TiFeMn alloy [6] powders were alternatively mixed with Mg powder. The best reported result was achieved by Kondo et al [7]. The authors have milled Mg and $TiFe_{0,9}2Mn_{0,08}$ (50/50 wt.%) in a planetary ball mill (Fritsch, Pulverisette 7), with some n-hexano, at 600 rpm during 80h. After a long heat treatment the composite absorved ~3.3 wt.% of hydrogen at 298K (1.55 MPa) after 20h. Desorption ocurred at 573K. In other investigations nanometric nickel (n-Ni) [8] or multi-walled carbon nanotubes (MWCNTs) [9] were added to the MgH_2 + TiFe composites. In both investigatoins the authors obtained good capacities (higher than 4.5 wt. % of H2) but at higher absorption /desorption temperatures (above 540K). More recently Chen et al. [10] have also used CNTs but on Mg+TiFe composites. Astonishing capacity was obtained (6.6 wt.%) but at 423K. The results of the laters works have emphasized the important role of a high dispersion grade of TiFe particles (nanoparticle dispersion) for the absorption/desorption properties and the necessity of activating the composite by heat treatment cycling.

In this work we investigated the synthesis of MgH_2-TiFe composites aiming to produce a material capable to absorb hydrogen at room temperature without adding a third material for enhance catalysis and also preventing heat treatments for activation after milling.

Experimental

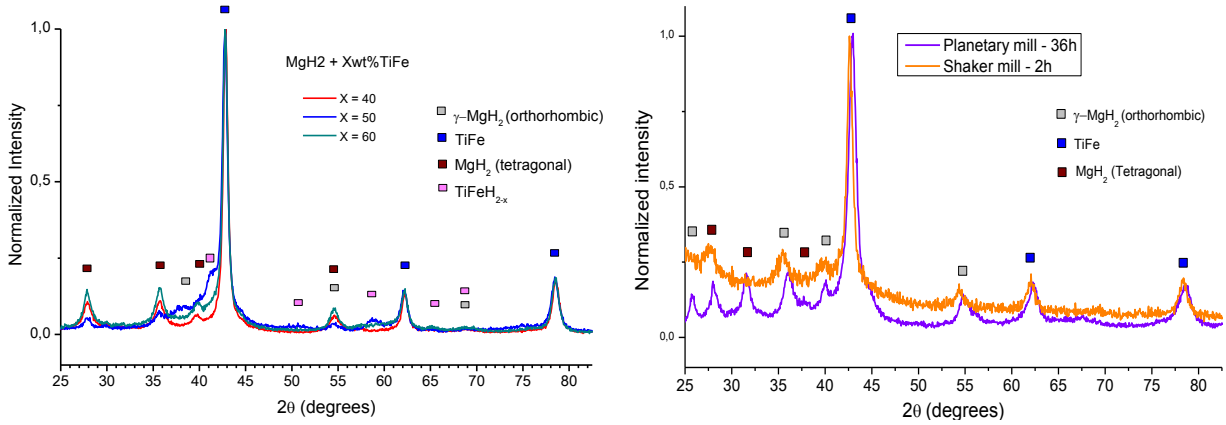
Commercial MgH_2 (purchased from Alpha Aesar, 98% pure, the balance being magnesium) instead of Mg powder was used in order to reduce adherence on the vial and balls. TiFe powder was produced by ball milling a mixture of TiH_2 and Fe powders followed by a reaction synthesis at 873K under vacuum. The full procedure for TiFe synthesis were described previously [11]. MgH_2 and TiFe powders were co-milled under high-purity argon atmosphere in order to produce MgH_2-X wt.% TiFe composites. Two sets of experiments were done. In the first set, a planetary ball mill (Pulverisette 6 - FRITSCH) was used to process compositions equivalent to X = 40, 50 and 60 (wt.% TiFe). Each milling charge consisted of balls (∅= 8 mm) made of tool steel and 10g of powders mixture, being the ball-to-powder weight ratio equal to 20:1. A cylindrical rounded-bottom vial, made from hardened steel and built in-house (vol. ~ 250 cm3), was used for planetary milling, always operated at 300 rpm during 6h. Milling times were further varied from 6 to 36 h (only for X = 40). Only one powder charge was carried out in this case. After each desired time, milling was paused and a small aliquot was taken for characterization. In the second set of experiments, milling was conducted on a shaker mill (SPEX - 8000M) at 1200 rpm, only for 2 hours and adding cyclehexane as process control agent. Balls and vial were made from tool steel. Ball to powder ratio was 30/1. Powders were handled in glove box with purified argon atmosphere during charge and discharge operations in order to guarantee an inert atmosphere inside the vials and to prevent burning of the milled products.

Milled composites samples were characterized by SEM and XRD (Cu-Kα radiation) analysis. SEM analysis of the composite powders was performed on samples mounted with epoxy castable resin. Low amount of hardener was used for preventing reaction with magnesium hydride, extending cure time (typically over 10h). Grinding and polishing steps were done manually, following standards procedures. Alcohol was used instead of water to prevent reaction with magnesium hydride during grinding. Hydrogen absorption kinetics measurements of the as-milled samples were conducted on an Sieverts' type apparatus (volumetric method) at room temperature.

The samples were first heated at 623K under vacuum for hydrogen desorption from MgH_2. Samples were then cooled to room temperature and further pressurized at 2MPa of hydrogen (99.998% pure). Hydrogen content (wt.%) was calculated from pressure drop in calibrated work volume.

Results and Discussion

Powder diffraction patterns of the as-milled samples is shown on Fig. 1. No reaction between TiFe and MgH2 was observed. Some orthorhombic MgH2 (gamma phase) was detected as a result of the high compression stresses during milling.



(a) planetary mill (milling time = 6h)

(b) MgH2 + 40wt.%TiFe

Fig. 1 - Powder diffraction patterns from as-milled composites

SEM micrographs of as-milled samples from the first set of experiments were shown in Fig 2 (b to e). Starting TiFe powder particles were aggregated due to reaction synthesis from TiH_2 e Fe powders (Fig. 2a). After milling for 6h (planetary mill), TiFe particle size seemed to be barely reduced (Fig. 2b). This can be seen by comparing with particles from the small micrograph inserted in Fig. 2b, which is a detail from Fig. 2a adjusted to the same magnification. In spite of being two different micrographs (loose powder against cross section images of the particles) it is evident that the milling action after 6h was poor. TiFe particle size reduction was impaired by MgH_2 matrix which has higher volumetric fraction. MgH_2 is brittle and absorbs the impact of the balls. After milling for 36 h finer dispersion was obtained but some particles of ~ 5 μm still remain.

Strong particle reduction was obtained in the second set of experimentes by using a shaker mill for 2 hours and adding cyclohexane as process control agent. Particle reduction was more homegeneous, i.e. the range of particle size are clear more narrow than that obtained after planetary milling.

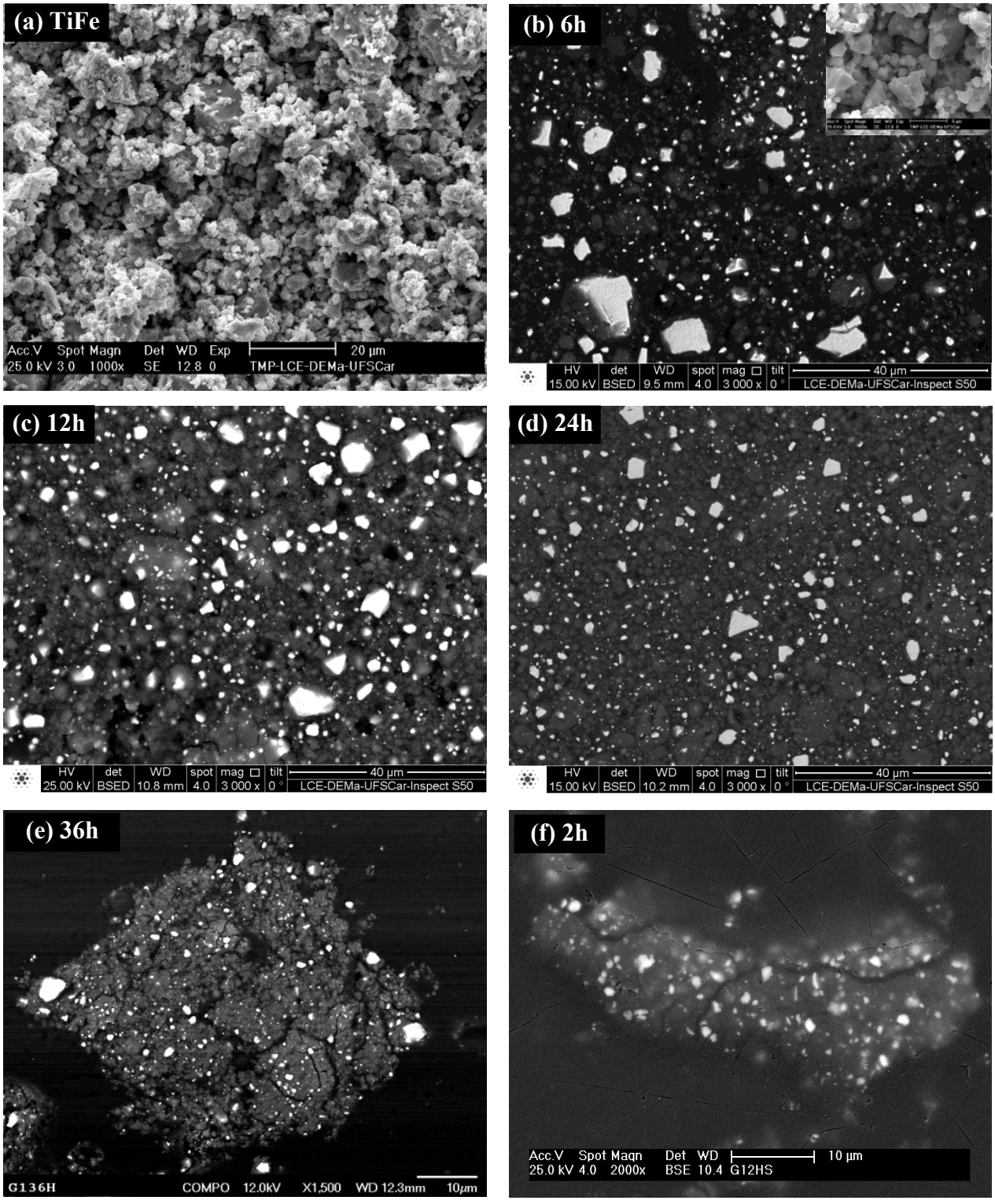


Fig. 2 - SEM micrographs: (a) secondary electron image from starting TiFe powder; (b) to (f) back-scattered electrons images from polished section of as-milled composite powder; (b) to (e) planetary mill; (f) shaker mill. Small micrograph superposed in (b) is a detail from (a) adjusted to the same magnification. Milling times are indicated. (Gray phase = MgH_2; White phase = TiFe)

Fig. 3 shows the results of absorption kinetics measurements of as-milled composites (X=40) after 36 h (planetary mill) and 2 h (shaker mill). Planetary milled sample has faster kinetics at the start of experiment than shaker sample. 3 wt. % of hydrogen was absorbed after 1 h by planetary milled sample. Higher dispersion degree of the TiFe particles after 36 h in the planetary mill (Fig. 2e) can explain that behavior, according to previous reports [8-10]. Higher hydrogen capacity was however attained by shaker milled sample after 5 h of absorption reaching almost 4 wt.% after 13 h

against 3.7 wt.% from planetary milled sample, both which better than the results from Kondo et al. [7]. The procedure of taking aliquots of planetary milled sample during milling impaired, apparently, the hydrogen intake, since the vial was open 3 times before (at 6, 12 and 24 h). In spite of using a glove box under high purity argon, the risk of even small oxygen contamination cannot be discarded.

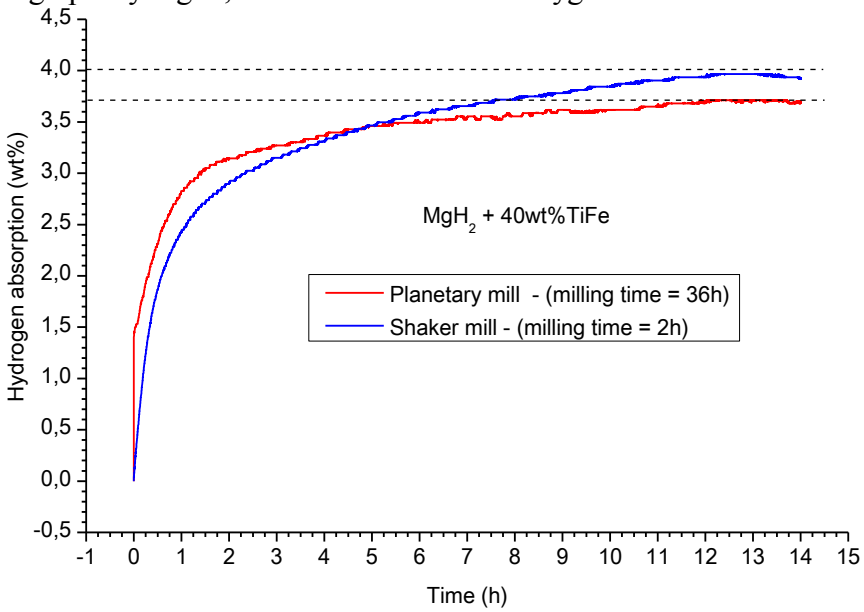


Fig. 3 - Absorption kinetics measurements at room temperature of as-milled composite samples

Conclusions

On the synthesis of MgH_2-TiFe composites by co-milling of the powdered phase materials, it has been found that milling of TiFe particles, critical for attaining very fine dispersion degree, was impaired by the magnesium hydride matrix. By increasing milling time or using higher energy ball mill (as shaker mill) a fine dispersion can be achieved. The best hydrogen kinetics (3 wt% at the first hour) was attained by the composite sample prepared in the planetary mill for 36 h. Higher hydrogen capacity was observed however for the sample milled in the shaker mill (4.0 wt.%), but only after 13 h. Additional experiments are currently been done, like performing a previous milling of TiFe particle before the co-milling and also carrying out Pressure-Compostion Isotherm measurements.

Acknowledgements

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