THE COMPOSITES OF MAGNESIUM HYDRIDE AND IRON-TITANIUM INTERMETALLIC

Varin R.A.[(1)]*, **Zaranski Z.**[(2)], **Czujko T.**[(3)], **Polanski M.** [(2)], **Wronski Z.S.**[(1,3)]

[(1)]Department of Mechanical and Mechatronics Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

[(2)]Department of Advanced Materials and Technologies, Military University of Technology, Kaliskiego 2, 00-908 Warsaw, Poland

[(3)]CanmetENERGY, Hydrogen, Fuel Cells and Transportation Energy, Natural Resources Canada, 1 Haanel Dr., Ottawa, Ontario, Canada K1A 1M1

Fax: 1-519-885-5862   E-mail: ravarin@uwaterloo.ca

Introduction

A lack of viable hydrogen storage system is a formidable barrier to the implementation of the Hydrogen Economy into automobile industry. Solid state hydrides with high gravimetric hydrogen capacities exceeding 6 wt.% are potentially very viable hydrogen media for on board storage. Among them, magnesium hydride (MgH_2) has quite high theoretical gravimetric hydrogen capacity (7.66 wt.%) and is widely available but its desorption temperature is too high and hydrogen desorption kinetics are too slow [1]. It has recently been shown [1,2] that by compositing high-and low-desorption temperature hydrides, the decomposition temperature of high-desorption temperature constituent obeys the rule of mixtures (ROM) very well known for engineered structural composites. In the present work the composite approach is applied to the $MgH_2+FeTiH_{\sim2}$ system. The FeTi intermetallic powder was obtained by melting and grinding of solidified ingots. Ground powder was pre-milled in hydrogen under ~700kPa pressure for 5h to achieve the synthesis of $FeTiH_{\sim2}$ and than mixed with MgH_2. The composites with various volume fractions of both constituents were processed by controlled mechanical milling (CMM) in hydrogen under ~400 kPa pressure in a magneto-mill. Hydrogen desorption was tested by using a Differential Scanning Calorimeter (DSC) as well as thermogravimetric and volumetric analyzer (Sieverts-type apparatus).

Results and discussion

Figure 1 shows the variation of particle size of MgH_2+FeTi as a function of milling time (particle size was calculated as the particle Equivalent Circle Diameter, $ECD=(4A/\pi)^{1/2}$, where A represents the projected particle area which was measured from SEM pictures). It is clearly seen that ball milling is very effective and the particle size of MgH_2 decreases rapidly with milling time reaching 1-2 μm after about 5 h of milling.
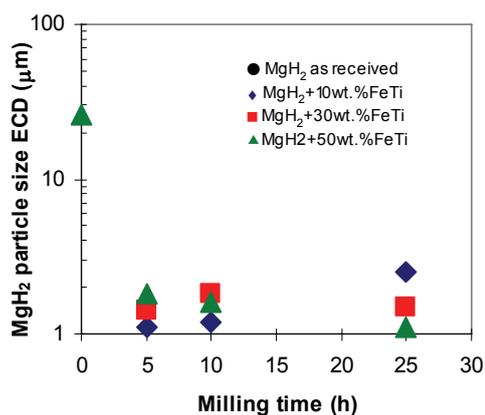

Fig.1. Average particle size of MgH_2 in composites MgH_2+X wt.% FeTi as a function of milling time.

Figure 2 shows the hydrogen desorption peak temperature of MgH_2 composited with FeTi obtained from respective DSC traces (not shown here) as a function of the content of FeTi for composites milled for 5, 10 and 25h. Despite some scatter of experimental results for various milling times it is clear that the desorption temperature of MgH_2 decreases linearly with increasing content of FeTi in a composite. The coefficient of fit R^2 for a linear dependence is ~0.73. This behavior seems to conform to the rule of mixtures (ROM) behavior as proposed for hydrides in [1,2]. However, the hydride $FeTiH_{\sim2}$ is a typical low temperature hydride whose equilibrium temperature at 1 bar H_2 pressure is reported as being equal to about -8°C (below zero) [1,3]. Therefore, it is most likely that during milling the newly formed $FeTiH_{\sim2}$ decomposes to FeTi and hydrogen gas. From this stand point, a continuous decrease of the desorption peak temperature of MgH_2 composited with FeTi in Fig. 2 can be interpreted as a catalytic-type effect of the FeTi intermetallic rather than its hydride. The underlying mechanism of the behavior observed in Fig.2 is now being scrutinized more thoroughly.
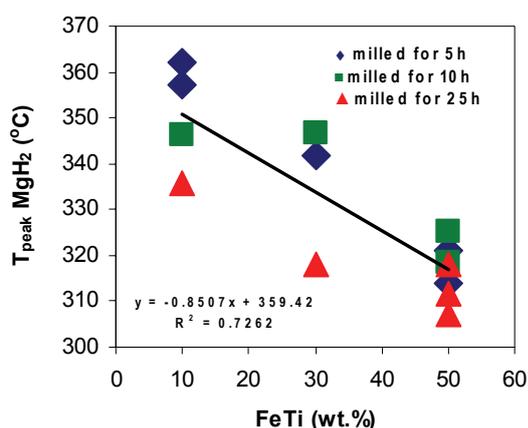
Fig.2. Hydrogen desorption peak temperature of MgH_2 composited with FeTi as a function of FeTi content for 5, 10 and 25h ball milling time.

Unfortunately, a substantial reduction of the desorption temperature of the MgH_2 constituent composited with FeTi is accompanied by a continuous decrease of hydrogen desorbed from a composite with increasing content of FeTi as shown in Fig. 3. Taking into account the fact that even for such a large content of FeTi as 50 wt.% the desorption temperature of MgH_2 is still slightly over 300°C the hydrogen capacity loss down to ~3 wt.% is too high to be considered practical.
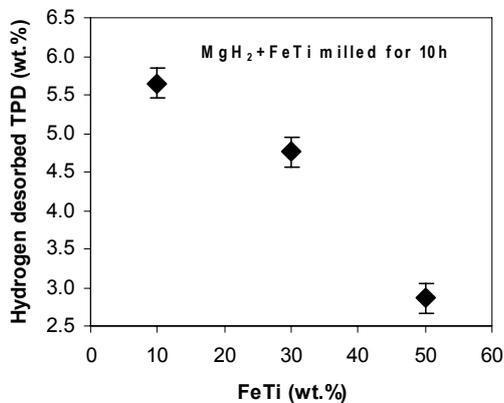

Fig.3. Hydrogen capacity desorbed in temperature
Programmed Desorption (TPD) tests as a function of FeTi content in the MgH_2+FeTi composites milled for 10h. The average values and standard deviation bars for capacity are calculated from

tests at the heating rates of 2, 5, 10, 15, 17.5, 20 and 25°C/min.

Conclusions

Composites of MgH_2+X wt.% FeTi, where X=10, 30 and 50 were synthesized by ball milling. Just after 5h of milling the average particle size of MgH_2 is reduced to 1-2 μm. It is observed that the hydrogen desorption temperature peak of MgH_2 in the MgH_2+FeTi composites seems to decrease linearly with increasing content of FeTi. Most likely, the observed behavior is owing to a catalytic effect of FeTi exerted on MgH_2. However, the hydrogen capacity of the MgH_2+FeTi composites is greatly reduced with increasing content of FeTi. For example, for the composite MgH_2+50 wt.% FeTi the desorption temperature of MgH_2 is reduced to slightly above 300°C while its hydrogen capacity is simultaneously reduced to ~3 wt.% which seems to be rather impractical.

References

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