Hydrogen storage in magnesium hydride doped with niobium pentaoxide and graphite

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Magnesium hydride powders mixed with 0.5 mol % of niobium pentaoxide with and without the addition of 1 wt % graphite have been treated by ball milling in argon atmosphere. Hydrogen absorption and desorption tests, as well as pressure-composition-isotherms (PCI), have been obtained on the treated material by means of a Sievert volumetric device operating in automatic cycling mode. The results indicate that the niobium pentaoxide addition to magnesium hydride improves the gas-solid reaction kinetics, in agreement with recent current literature. Further improvement of the absorption/desorption kinetics comes from addition of graphite. It seems that the thermodynamics of hydride formation is not influenced by these additions.

1. Introduction

Hydrogen is the ideal "fuel" for 21th century, not toxic and without pollution products resulting from combustion. The big problem for automotive purposes is the hydrogen storage in as little volume as possible. Light metal hydrides have higher volumetric content of hydrogen compared with gaseous and liquid hydrogen. Very promising hydrides are based on light metals as magnesium, MgH_2 having theoretically a hydrogen storage capacity of 7.6 wt %. Unfortunately MgH_2, like other light metal hydrides, shows slow kinetics of hydrogen absorption/desorption. This, according to Buschow et al. (1982), is mainly because MgH_2 is very stable, having a high enthalpy of formation ($\Delta H = -75$ kJ/mol) and a very low plateau pressure at ambient temperature (about 0.0001 atm). In order to improve the hydrogen absorption/desorption kinetics, several authors have used the ball milling technique to mix MgH_2 with transition metals, Liang et al. (1999) and Bobet et al. (2002), or transition metal oxides, Oelerich et al. (2001), or graphite, Huot et al. (2003), Dal Toé et al. (2004). Very recently, Barkhordarian et al. (2004) proved that Nb_2O_5 is the most effective catalyst, among those studied up to the date, for improving hydrogen absorption/desorption kinetics of MgH_2. Therefore, MgH_2 doped with Nb_2O_5 becomes an interesting hydrogen storage material at temperatures as low as 230÷250 °C. Starting from this point, we have studied the modification of hydrogen storage properties of ball milled MgH_2 and Nb_2O_5 mixture, due to the addition of small amounts of graphite.

2. Experimental details

Magnesium hydride powders (95 % MgH_2 + 5 % Mg, from Sigma-Aldrich) were mixed with 0.5 mol % of niobium pentaoxide Nb_2O_5 powders (99.99 %, from Aldrich Chem.) and ball milled in a SPEX8000 mill in argon atmosphere for 20 h with a ball to powder weight ratio of 10/1 (sample I). The milling time was lower than the 120 h used by Barkhordarian et al. (2004) because the shaker mill SPEX8000 is more efficient than the Fritsch P5 planetary mill used by them. A second sample was prepared by adding to the previous mixture in the mill vial 1 wt % of graphite powder (99.99 %, from Carlo Erba) and milling for the same time (sample II). XRD patterns were taken on the mixed powders using a PW1820/00 Philips apparatus equipped with the CuKα radiation.

Hydrogen absorption and desorption kinetics were studied at 280 °C using a commercially available volumetric Sievert apparatus supplied by AMC, Pittsburgh, recently set up in our laboratory. With the same equipment also pressure-composition-isotherms (PCI) measurements were taken in the temperature range 205÷337 °C.

Milling operations and handling of the samples have been performed in protective argon atmosphere.

3. Results and discussion

The phase composition after ball milling was analysed by X-ray diffraction as shown in Fig. 1 for sample II. The predominant phase obtained for this sample as well as for sample I is β-MgH_2. The other phases detected are γ-MgH_2 and Nb_2O_5. Small amounts of MgO and metallic Nb are also present in the samples. MgO produced during milling or sample handling is undesirable because it diminishes the hydrogen storage capacity of the material, but due to the high affinity of Mg with oxygen its presence is not completely avoidable. Carbon was not detectable due to its low concentration.
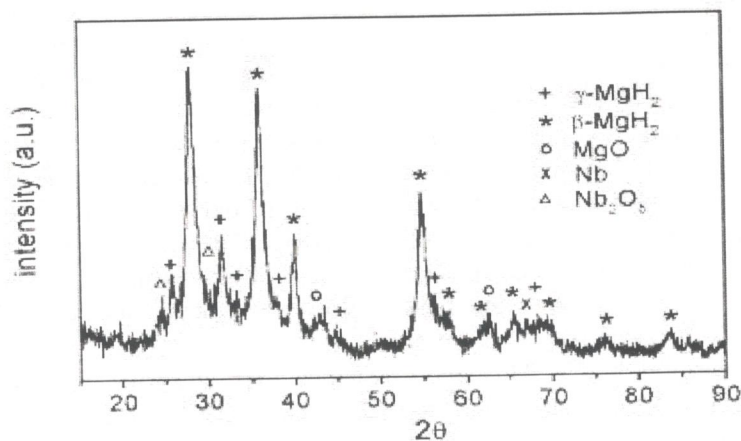

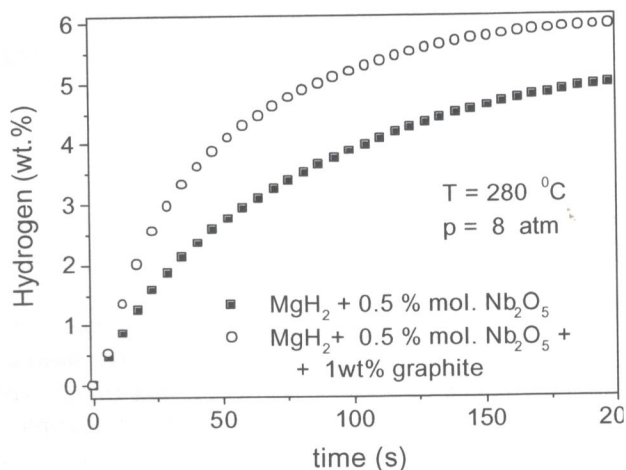Fig. 1 X-Ray diffraction pattern for sample II.

Fig. 2 Hydrogen absorption kinetics for studied samples.

Hydrogen absorption measurements at 280 °C and 8 atm of H_2 are presented in Fig. 2 for samples I and II. Sample II displays in the interval 0÷200 s a faster hydrogen absorption compared with sample I. Also, the maximum hydrogen content of sample II is 6.3 wt %, higher than the 5.5 wt % value obtained for sample I. In this figure the hydrogen content is shown relatively to the total weight of the samples (including Nb_2O_5 and graphite). Sample II reaches 63 % of its hydrogen storage capacity in 50 s, 83 % in 100 s and 93 % in 200 s. Taking into account the presence of Nb_2O_5 and graphite, the theoretically maximum allowed hydrogen content of 7.6 wt % for pure MgH_2 lowers down to the theoretically maximum allowed 7.1 wt % for sample II. The difference between the experimental value of 6.3 wt %, found for this sample, and the theoretical one could be explained by the presence of MgO, which lowers the maximum allowed content of hydrogen and on the other hand hinders the hydrogen diffusion into Mg nanograins.

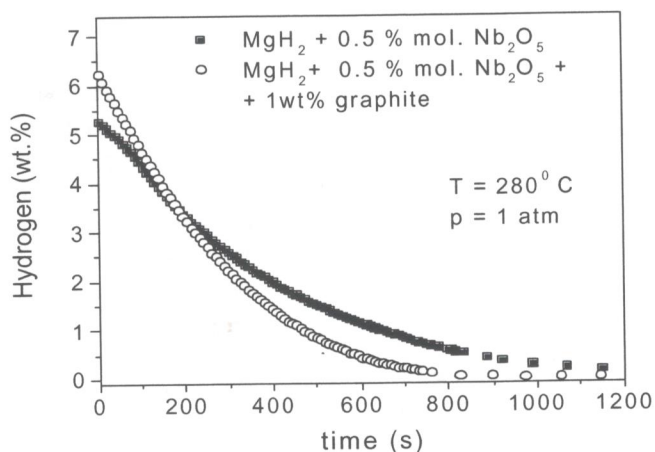Fig. 3 shows the hydrogen desorption kinetics for both samples at 280 °C and 1 atm of H_2. Also in this case the graphite addition improves the desorption kinetics. Sample II desorbs 47 % from the maximum hydrogen content in 200 s, 76 % in 400 s and 93 % in 600 s. The presence of graphite has an evident additional catalytic role on hydrogen absorption /desorption processes. These results can be compared with kinetic data of Huot et al.
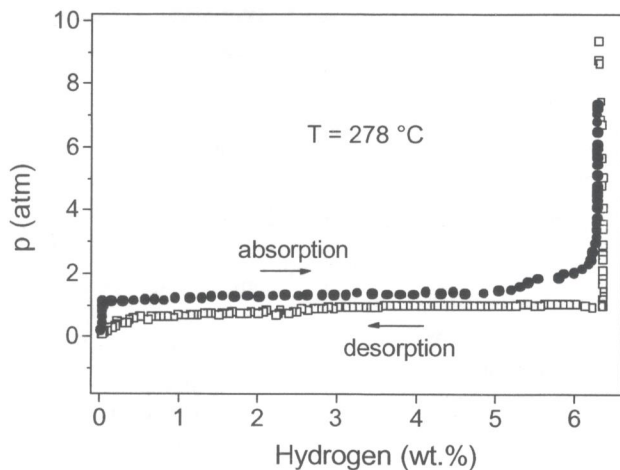

Fig. 3 Hydrogen desorption kinetics for studied samples.

Fig. 4 Pressure-composition-isotherms (PCI) at 278 °C for sample II.

(1999) regarding pure ball milled MgH_2, which absorbs and desorbs the same amount of hydrogen in much longer times (e.g. only 5 % of hydrogen content is desorbed in 600 s). Additionally, due to the higher maximum hydrogen content stored in sample II, one may argue that graphite reduces the magnesium oxide layer surrounding Mg nanograins, which is not well appreciated in the X-ray diffraction patterns due to the low intensity of the corresponding broad peaks. This reduction enhances the hydrogen diffusion into the nanograins, improving the absorption kinetics.

PCI measurements in absorption mode indicate that the plateau pressure in the temperature range 205÷337 °C varies between 0.15 to 6.15 atm. We performed also PCI measurements in desorption mode in the range 236÷337 °C with a corresponding plateau pressure between 0.24 and 4.82 atm. As an example, in Fig. 4 is given a PCI absorption-desorption cycle at 278 °C. The plateau pressure for PCI absorption (measured at the middle of the plateau) is 1.31 atm, higher than that obtained for PCI desorption, 0.94 atm.
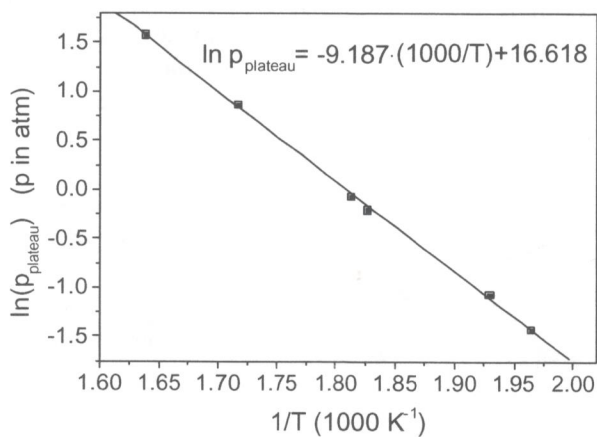

Fig. 5 Van't Hoff plot for sample II.

The slope of plateau pressure behaviour vs. reciprocal of temperature (Van't Hoff plot) allows us to obtain the enthalpy of hydride formation. The Van't Hoff plot for the PCI desorption mode of sample II is shown in Fig. 5. The enthalpy of formation results to be -76.3 ± 1.3 kJ/mol very close to -75 kJ/mol, as previously obtained for pure MgH_2 by Buschow et al. (1982). Taking into

account this result it seems that Nb_2O_5 and graphite addition do not modify the thermodynamics of hydrogen absorption/desorption of MgH_2.

4. Conclusions

Ball milling the MgH_2 + 0.5 % mol. Nb_2O_5 mixture with the addition of 1 wt % graphite improves the kinetics of hydrogen absorption/desorption. Graphite enhances the maximum hydrogen content by diminishing the magnesium oxide surface layer.

The enthalpy of hydride formation obtained from the Van't Hoff plot is -76.3 ± 1.3 kJ/mol, very close to the value of -75 kJ/mol, previously obtained for pure MgH_2. We may argue that Nb_2O_5 and graphite addition do not influence the thermodynamics of hydrogen absorption/desorption. Work is in progress to better clarify these aspects.

5. References

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