Hydrogen Sorption Kinetics and Mechanism in Mg-based Nanocrystalline Materials.

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As the use of fossil fuels leads to green house gas emissions and global warming and these are at the edge of its depletion, hydrogen presents a clean and efficient energy alternative based on renewable energies. With respect to the difficulties in storage and transport of hydrogen (low density and liquefaction point, high reactivity) metal hydrides offer a safe and effective medium of hydrogen and can be used in fuel cells, metal-hydride batteries, thermal engines, air-conditioning systems and other environment-friendly applications. Among these hydrides, Mg-based metal hydrides are excellent candidates, since Mg can theoretically pick up 7.6 wt. % of H_2 and is of low cost. Its limitation for practical application however lies in the slow hydrogen sorption kinetics due to the high thermodynamic stability of its hydride. In the present communication we review our recent contributions to understand and to improve the hydrogen sorption kinetics in Mg-based nanocrystalline materials.

In the first studies significant progress was done by using nanocrystalline MgH_2 powders produced by high energy ball milling [1,2] as compared to bulk polycrystalline Mg. In fact a crystallite size reduction and the formation of grain boundaries and microstructural defects are producing pathways for a favourable H_2 charge/discharge process. In this regard we have prepared nanocrystalline Mg and MgH_2 materials by the gas phase condensation (GPC) method [3], showing very small particle sizes as compared to the material obtained by ball milling (see Figures 1a and 1b). The kinetic study shown in Figure 2a indicates how the reduction of crystallite and particle size is improving the hydrogen sorption kinetics. Nevertheless the decrease in particle size is also producing a higher surface oxidation of the material what presents a diffusion barrier for hydrogen and produces a decrease in the hydrogen storage capacity (see Figure 2a).

The addition of additives, mainly transition metals and oxides, during ball milling of MgH_2 introduced also a big improvement in the hydrogen sorption kinetics [4]. Nb_2O_5 was one of the best additives found. However the mechanism by which these oxides are improving the kinetics was not clear. Here we present our results indicating the formation of ternary Mg-Nb-O phases [5] that during migration to the surface produce "pathways" allowing the easy diffusion of hydrogen into the Mg nanocrystals. In Figures 1b and 1c we show the Transmission electron (TEM) micrograph images for MgH_2/Nb_2O_5 materials obtained by ball milling of MgH_2 together with the oxide phase additive in the form of micro- and nano-crystalline powder respectively. The hydrogen sorption analysis shown in Figure 2b indicates how very short milling times are necessary with the nanocrystalline additives to obtain important kinetic improvements [6]. In this work we emphasize the key role of using nanocrystalline additives to make process available for technical applications.

References:

[1] A. Zaluska, L. Zaluski, J.O. Strom-Olsen, Journal of Alloys and Compounds 288 (1999) 217-225.
[2] K.J. Gross, P. Spatz, A. Zuttel, L. Schlapbach, Journal of Alloys and Compounds 240 (1996) 206-213.
[3] O. Friedrichs, L. Kolodziejczyk, J.C. Sánchez-López, C. López-Cartés, A. Fernández, *Journal of Alloys and Compounds (2005) submitted.* EnergyEnergy

[4] W. Oelerich, T. Klassen, R. Bormann, Journal of Alloys and Compounds 315 (2001) 237-242.
[5] O. Friedrichs, F. Aguey-Zinsou, J.R.A. Fernandez, J.C. Sanchez-Lopez, A. Justo, T. Klassen, R. Bormann, A. Fernandez, Acta Materialia 54 (2006) 105-110.
[6] O. Friedrichs, T. Klassen, J.C. Sanchez-Lopez, R. Bormann, A. Fernandez, Scripta Materialia (2006) In Press, Corrected Proof.

Figures:

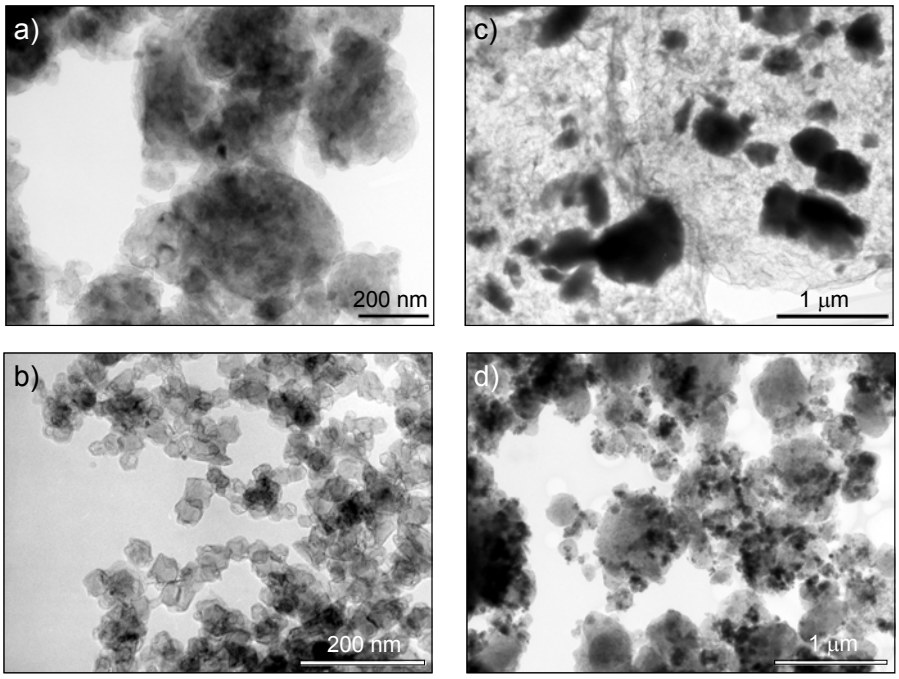

Fig. 1: TEM micrographs of a) ball milled MgH_2, b) MgH_2 as obtained by GPC, c) MgH_2 milled with micrometric Nb_2O_5 and d) MgH_2 milled with nanometric Nb_2O_5.

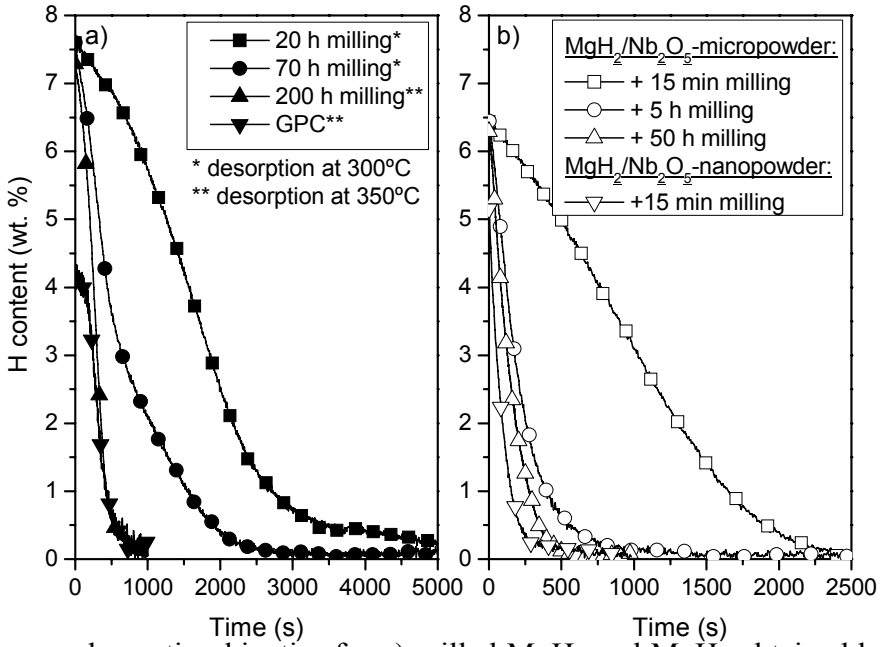

Fig. 2: Hydrogen desorption kinetics for a) milled MgH_2 and MgH_2 obtained by GPC and b) Premilled MgH_2 (20 h) additionally milled with micro and nanometric Nb_2O_5.

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