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Pellets of MgH_2-based Composites as Practical Material for Solid State Hydrogen Storage

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1 Introduction

MgH_2 is one of the most studied materials among those able to store hydrogen in solid state, having many assets in its favour, like low cost, abundance, light weight and a theoretical storage capacity of 7.6 wt%. However, concerning the practical applications, it has the limitations of high thermodynamic stability and slow hydrogen absorption/desorption (a/d) kinetics. To come out of these practical shortcomings MgH_2 is used in nano-crystalline form obtained by high energy ball milling mixed with transition metal oxides, e.g. Nb_2O_5 [1,2], acting as catalysts to improve the hydrogen a/d kinetics with little reduction in the gravimetric capacity. During scaling up studies of MgH_2 based powders in a specially designed reactor it was observed that the hydrogen storage capacity, as well as the a/d kinetics, decreased with the ongoing cycles [3]. It was argued that this degradation was due to a close compaction of the powder particles inside the reaction chamber associated with local overheating, with the detrimental effect of strongly reducing the free flow of hydrogen through the storage material. The compaction of the powders was probably due to a pressure gradient that built up during the first stages of hydrogen absorption process given by the difficult gas transport through the Mg bed. These observations motivated us to study MgH_2 based powders moderately pressed in the form of pellets with the addition of some binding agent in order to retain stable mechanical consistency and structure with persistent free paths for hydrogen diffusion. The use of pellets instead of powder should improve the hydrogen transport inside the storage vessel avoiding pressure gradients and further compaction of the material. Moreover, in principle, each pellet should behave as an independent system reducing scaling up effects on the a/d kinetics.

In this work we have tested MgH_2 catalysed ball milled powders mixed with Al powder as a binder pressed with an electro-mechanical press, following an approach already preliminarily tested [4]. The crystalline structure, the hydrogen a/d properties and the mechanical strength of the samples have been analysed before and after hydrogen a/d cycling. The incorporation of aluminium is supposed also to enhance the thermal conductivity in the pellets.

2 Experimental

MgH_2 powder mixed with Nb_2O_5 (5 wt %) and graphite (1 wt%), as catalysts of the gas-solid reaction, was ball-milled in a SPEX 8000 shaker mill for 20 hours using steel balls with ball to powder ratio of 10:1 (samples denoted as cat-MgH_2). Two types of pellets were studied: one made up of as-milled cat-MgH_2 powder and in the other case 5 and 20 wt% of Al powder was homogenously mixed by ball-milling for 5 min with cat-MgH_2 to act as a binding agent (samples denoted as cat-MgH_2-Al5 and cat-MgH_2-Al20, respectively). All pellets were obtained by pressing the powders in Ar atmosphere with a uniaxial pressure of 180 MPa by means of an Instron 1121 tester. Kinetic and thermodynamic tests were performed using a Sievert's type gas reaction controller. Annealing of samples containing Al powder was performed at 450 °C in the same Sievert's apparatus for 10 min under a rotary pump vacuum before starting the hydrogen a/d cycles. In order to test the compressive strength resistance of the pellets after different a/d cycles, compression tests were performed using the same Instron 1121 tester at the compressive strain rate of 1 mm/min. For all samples the hydrogen release processes were performed at the temperature of 320°C and H_2 pressure of 1.2 atm, while the soak processes were performed at the same temperature and H_2 pressure of 15 atm.

3 Results and Discussion

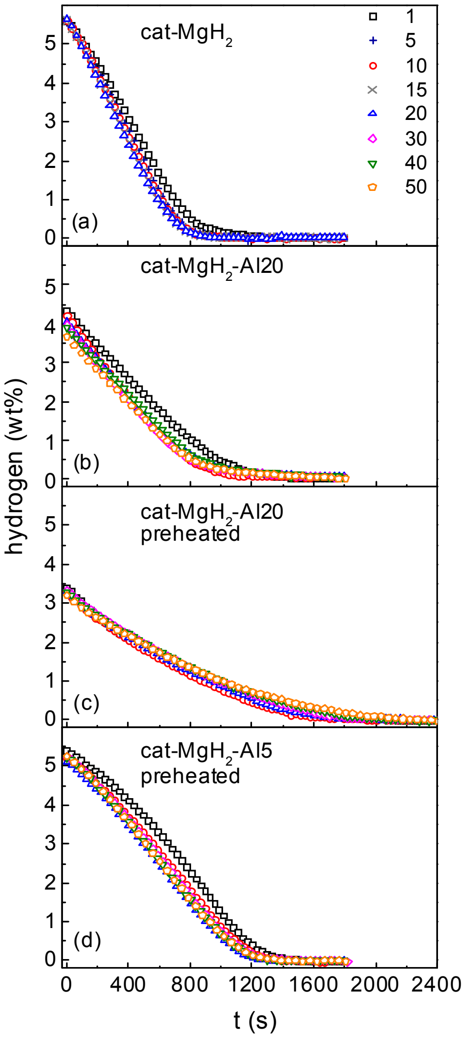

Figure 1: Desorption cycles of pellets cat-MgH_2 (a), cat-MgH_2-Al20 without preheating (b), cat-MgH_2-Al20 with preheating (c) and cat-MgH_2-Al5 with preheating (d).

Figure 1a) shows the release kinetics for the pellet of cat-MgH_2 and indicates that the maximum stored and released hydrogen in this case was 5.6 wt %, which remained stable for all the hydrogen a/d cycles. During cycling, the pellet lost gradually its mechanical consistency and after 20 cycles got completely powdered. This behaviour is in agreement with the observed continuous reduction of desorption time by cycling, considering that a not close compacted powder favours the hydrogen flow through the material. The breaking of the pellets is due to the stress induced during absorption with an increase of 32% of the volume for the host Mg forming MgH_2.

Figure 1b gives the desorption curves for pellet cat-MgH_2-Al20, where is shown that the hydrogen content goes from the initial 4.3 wt% to about 3.6 wt% after 50 cycles. This decrease can be explained in terms of Mg-Al phases formation during cycling, slowly reacting with hydrogen due to a higher plateau pressure with respect to pure Mg. The compactness of this pellet started degrading before 20 cycles and was completely lost before 50 cycles. Another similar pellet was then first heated in vacuum at 450 °C, for 10 minutes, in order to facilitate the formation of some intermetallic phases and/or solid solution and then submitted to 50 a/d cycles. As shown in figure 1c, the maximum hydrogen content of this pellet was about 3.3 wt% and the time for 90% desorption increased to 1320 s. The hydrogen content was now almost constant under cycling, in contrast to the pellet without pre-heating, and the degradation of mechanical compactness resulted less. However, the pellet started to degrade before about 50 cycles. Cat-MgH_2-Al5 pellets were cycled under similar conditions after pre-heating as in the previous case. Figure 1d shows that in this case almost all the absorbed hydrogen (5.3 wt%) was released in about 1500 s. The desorption behaviour became almost stable just after 10 cycles and the pellet remained mechanically consistent and hard even after 50 cycles.

The XRD measurements of cat-MgH_2-Al5 and cat-MgH_2-Al20 hydrogenated and dehydrogenated pellets after heat treatment and 50 hydrogen a/d cycles give the relative abundance of the phases, estimated by means of the Rietveld refinement, reported in Table 1. These results agree with the study of hydrogenation process of ball milled Mg-Al powders by Crivello et al. [5,6], which occurs in two completely reversible steps:

$$Al_{12}Mg_{17}+9H_2 \leftrightarrow 9MgH_2+4Al_3Mg_2 \qquad (1)$$

$$4Al_3Mg_2+8H_2 \leftrightarrow 8MgH_2+12Al \qquad (2)$$

Reaction (2) did not reach completion in our operating conditions, probably due to the higher relevant plateau pressure. The estimated amount of Al (4 wt%) in the cat-MgH_2-Al20 hydrogenated sample is larger than in the case of dehydrogenated sample. This is due to the fact that a certain amount of Al is in solid solution in the structure of Mg and during hydrogenation is expelled, according to the disproportionation reaction

$$Mg(Al_x) + H_2 \leftrightarrow MgH_2 + xAl \qquad (3)$$

Table 1: **Results of Rietveld refinement of the XRD patterns of the cycled pellets.**

Sample	β-MgH_2 (wt %)	Mg (wt%)	MgO (wt %)	Al (wt %)	Al_3Mg_2 (wt %)	$Al_{12}Mg_{17}$ (wt %)
cat-MgH_2-Al20 450 °C (dehydrogenated)	<2	39	14	<3	-	43
cat-MgH_2-Al20 450 °C (hydrogenated)	51		17	4	15	13
cat-MgH_2-Al5 450 °C (dehydrogenated)	5	73	22	-	-	-
cat-MgH_2-Al5 450 °C (hydrogenated)	72	7	18	<3	-	-

According to the Mg-Al phase diagram, the small amount of Al is not sufficient for the precipitation of the eutectic phase and leads only to a solid solution of Al in Mg. The presence of Al in solid solution is also supported by the fact that the estimated amount of Al in the dehydrogenated sample is negligible.

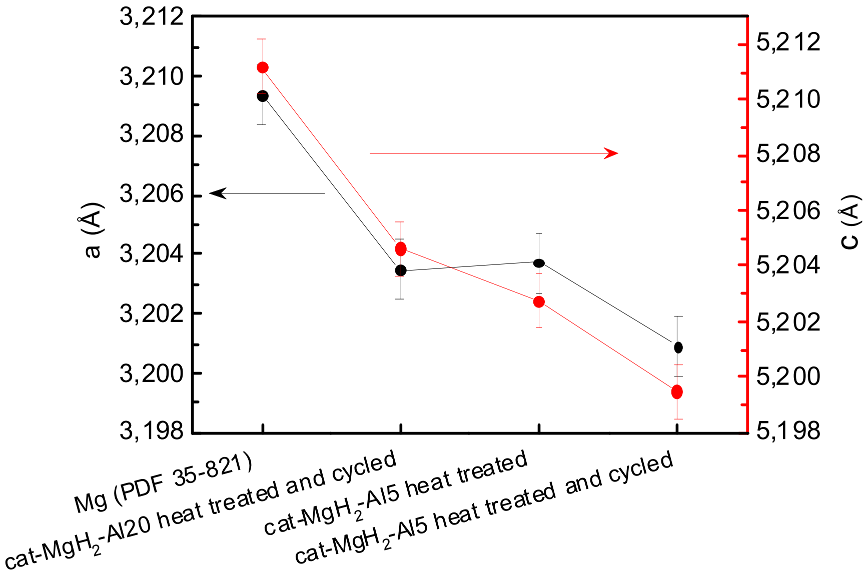

Figure 2: **Lattice parameters of Mg estimated by Rietveld refinement for some of the studied dehydrogenated samples.**

The lattice parameters of Mg obtained by the Rietveld refinement for some of the dehydrogenated samples are shown in Figure 2. These values are smaller compared to those of pure Mg and this is certainly due to the presence of Al in Mg(Al) solid solution, considering the smaller metallic radius of Al compared to that of Mg. The smallest lattice parameters are observed for the cat-MgH_2-Al5 sample after heat treatment and 50 a/d cycles, which shows that in this case Al prefers to enter in the Mg(Al) solid solution instead of forming Mg-Al intermetallic phases. On the contrary, in the case of the cat-MgH_2-Al20 sample the precipitation of the eutectic phase $Al_{12}Mg_{17}$ slows down the formation of Mg(Al) and the lattice parameters of Mg are larger.

Figure 3 shows the results of the mechanical tests for hydrogenated pellets without Al and with 5 wt% Al after 0 and 50 a/d cycles. It is evident the better behaviour of pellets containing Al, while, in absence of aluminium, a stress of 30.1 N/mm^2 and of 8.1 N/mm^2 was sufficient to break the pellet after 10 and 20 a/d cycles, respectively. As said before, it was not possible to recover the pellet after 50 a/d cycles. The better behaviour of samples containing Al can be attributed to the presence, according to reaction (3), of an Al matrix surrounding the MgH_2 particles. Anyway, also in this case the strength decreases, likely due to the progressive increase of porosity: 43.7 N/mm^2 and 13.9 N/mm^2 after 20 and 50 cycles, respectively.

Work is in progress to better understand, with a high resolution investigation, the micro-structural evolution of the pellets in the different stages of a/d cycling. Moreover, the preparation of a small vessel to study the hydrogen a/d behaviour of a metal hydride in form of pellets instead of powder, in order to overcome the shortcomings of the scaling up effects, is under way.

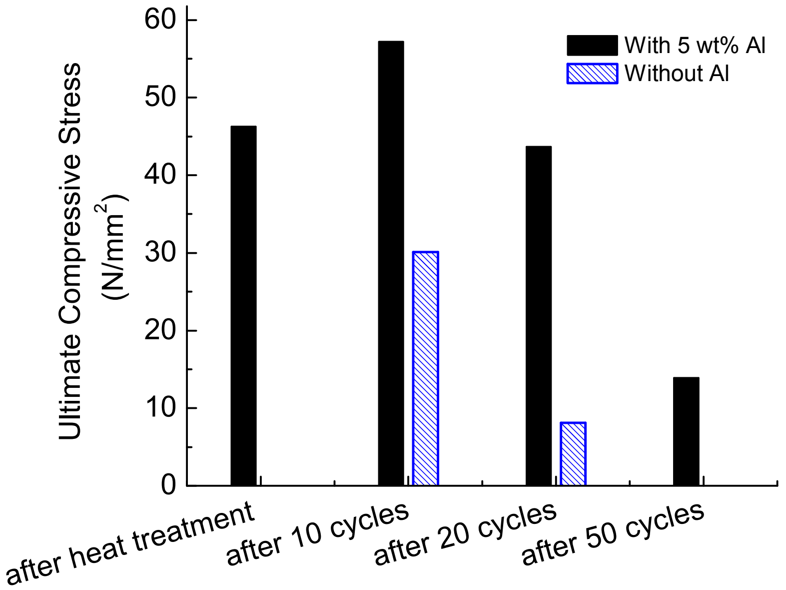

Figure 3: **Results of the compression tests to estimate the mechanical strength of the pellets without and with 5 wt% Al.**

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