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Performance tests of a small hydrogen reactor based on Mg–Al pellets

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ABSTRACT

On the basis of a previously acquired experience on scaling up issues concerning the use of magnesium hydride as a base material for solid-state hydrogen storage, a small reactor was designed and tested in different operating conditions. It contains about 10 g of catalyzed magnesium hydride powder mixed with 5 wt.% aluminium powder and pressed in the form of cylindrical pellets and the heat flow is managed by means of an oil circulation system. Carbon paper is used to ensure good heat conductivity between the pellets and the inner wall of the reactor and between one pellet and another. A number of hydrogen absorption and desorption cycles at different temperatures and pressures was carried out to compare the behaviour of the small reactor with the laboratory data obtained on small amounts (fractions of grams) of powdered and pelletized samples. Data acquisition for gas flow, pressure and temperature in different positions of the reactor allow a good understanding of internal dynamics. The results in terms of hydrogen absorption/desorption kinetics and of stability to ongoing cycles are stimulating, so that the tested small reactor can be considered as a basic element for further studies and improvements.

1. Introduction

Scaling-up studies of magnesium hydride based powders in reactors as systems for solid state hydrogen storage have been recently reported [1,2], showing that the performances of those systems can degrade quickly with hydrogen absorption/desorption (a/d) cycles. The study started from a previously developed MgH_2-based composite material sintered in pellets, which showed good cycling behaviour and mechanical strength stability [3]. So, a small experimental reactor was conceived to evaluate the scale-up effects. The design of this first experimental reactor containing hydride pellets was based on simplicity in its realization and on the possibility to adopt a modular concept.

2. Experimental

The functional material was composed by MgH_2 powder (as-received from Th. Goldschmidt GmbH, 95% purity with residual 5% metallic Mg) mixed with 5 wt.% Nb_2O_5, 1 wt.% C and 5 wt.% Al. Niobium pentoxide improves the hydrogen a/d kinetics and graphite acts as a lubricant of ball milling [4]. Aluminium, which acts as a binder, was proved to increase the mechanical properties of pellets obtained by compaction of the powder [3]. The powder mixture was ball-milled for 20 h in a SPEX 8000 shaker mill using steel balls with a ball to powder ratio of 10:1. This operation mixes intimately the hydride with the additives and enhances the reactivity with hydrogen increasing the crystalline defects and specific surface area of the powder grains.

To avoid external contamination, the milling was carried out in special vials with a little overpressure of Ar and all samples were handled in a M-Braun LABstar MB10 compact glove-box with Ar atmosphere.

Pellets were obtained pressing the milled powder mixtures with a uniaxial pressure of 180 MPa by means of an Instron 1121 mechanical tester. The pelletizer was kept in Ar atmosphere and the load was applied with a constant displacement rate of 1 mm/min up to 180 MPa, then the level of strain was kept constant for 60 s and a second step of compression, under the same conditions of displacement rate and final pressure, was performed to compensate the partly reduced stress.

The pellets were having a mass of about 0.3 g and a cylindrical shape with diameter of 7 mm and height of 7 mm. They were thermally treated under rotary pump vacuum in a small furnace heated at 5 °C/min up to 450 °C for about 120 min. Batches of 12 pellets were used in this annealing operation after which a 10% mass loss was observed: this was due both to dehydrogenation and to some probable Mg alloy evaporation (the furnace chamber resulted coated by a thin layer of this metal).

The experimental reactor (Fig. 1) was composed of an AISI 304 steel pipe (outer diameter 12 mm, wall thickness 1.5 mm) inserted in a larger one of the same material (outer diameter 25 mm, wall thickness 2 mm). The interspace between the two pipes allowed heat exchange fluid to flow to control temperature. All the connections and the inlet valve were of Swagelok type. Opposite to the gas inlet three K thermocouples entered the inner pipe to measure the temperature of the pellets in different positions of the reactor during the test.

To improve the thermal conductivity between the pellets and between the pellets and heat exchanger, carbon mat from R&G Faserverbundwerkstoffe GmbH-Composite Technology was inserted between one pellet and another and wrapped around them. In order to insert the pellets inside the reactor in the correct position the extremities of the thermocouples were bent appropriately.

Automated facilities developed at the ERSE labs [2] and schematized in Fig. 2 were utilized to test the reactor: that allows performing hydrogen a/d cycles at desired temperatures, heating and cooling rate, gas flow rate and pressure. The test

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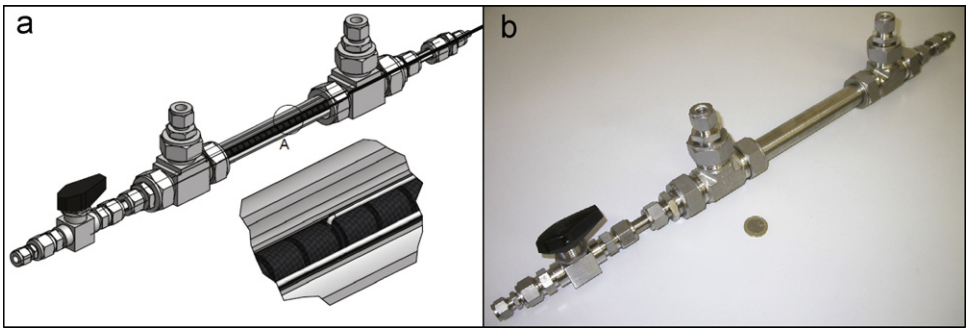

Fig. 1. Design sketch of the reactor representing a detail of inner placement of pellets (a) and picture of the same after manufacturing (b).

system had two different circuits. The gas circuit, equipped with control and measuring instruments (provided by Bronkhorst High-Tech B.V., El-Flow and El-Press series), shut and safety valves, was connected to the inner pipe of the reactor. The oil circuit, working with Solutia Therminol 72 oil and including oil reservoir, pump, expansion tank and electrical heater, was connected with the external pipe.

The reactor was inspected before and after 50 cycles of hydrogen a/d by means of radiographic equipment Bosello SRE80 MAN with a XRG130 IT generator, 0.2 mm focal spot and 19° aperture angle. Voltage and current values of 90 kV and 2.80 mA, respectively, were used as initial settings and slightly adjusted to optimize the contrast.

3. Results and discussion

Once the reactor had been connected to the test device, the first operation was hydrogen absorption, because during the heat treatment the pellets were dehydrogenated as a result of combined action of temperature and rotary pump evacuation.

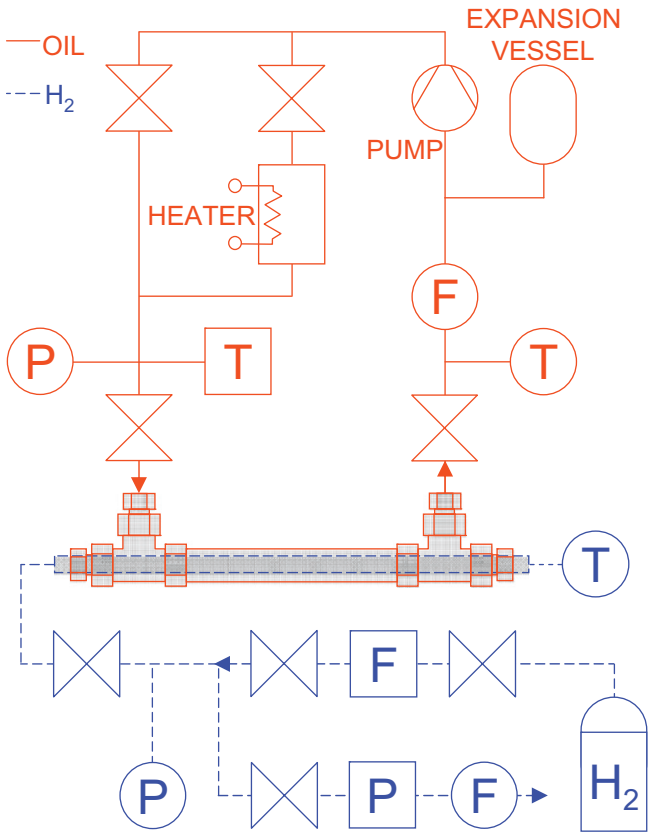

Fig. 2. Simplified schematic drawing of the experimental setup coupled with the reactor. Circles are measuring instruments and squares are measuring and control instruments. Letters F, T, and P indicate flow, temperature and pressure, respectively.

The first a/d cycles were operated manually to test the effectiveness of the chosen operating parameters, and then the automatic mode started.

In absorption mode the operating values were the following: hydrogen pressure 8 bar, flow rate between a maximum of 0.7 Nl/min and a minimum of 0.01 Nl/min, temperature 270 °C. The absorption started automatically when the established temperature was reached and the gas valve opened to let the chosen maximum hydrogen flow in the reactor. This lasted as long as the reaction kinetics slowed down and the gas flow decreased, then the flow rate was measured with the valve fully opened up to the moment when the minimum flow rate was reached. The amount of stored hydrogen was calculated from the flow rate measurements, while the difference between inlet and outlet oil temperatures, oil heat capacity and flow rate allowed the calculation of the heat generated by the exothermic absorption reaction.

The selected operating values for the desorption steps were: discharge hydrogen pressure of 1.2 bar, minimum hydrogen flow rate of 0.01 Nl/min and temperature of 310 °C. In these steps too, the operation started when the set temperature was reached: the hydrogen outlet valve opened and a pressure controller maintained the hydrogen pressure to the established value. As for absorption, the desorption lasted as long as the minimum hydrogen flow rate value was reached.

The instrumental flow data were elaborated to obtain the hydrogen wt.% vs. time plots shown in Fig. 3a and b. A comparison with the data measured for a single pellet [3] shows clearly that the desorption kinetics is worsen, but anyway better than for the scaling-up tests carried out with a reactor containing powder not previously pressed. These differences may be in part attributed to an inhomogeneous hydrogen gas flow and heat exchange rate in the scaled-up systems with respect to the single pellet experiments. The absorption behaviour in the present small reactor is similar to that of a single compacted pellet. We see that with the ongoing cycles the maximum hydrogen gravimetric capacity is stable, around 5.2 wt.%, but that desorption kinetics is slowing down. It is to be noted that the flow measurements and the thermal fluid heating, used in the present case, have different performances and settings compared to the Sieverts' apparatus and the electrical heating used to test a single pellet [3]. For instance, a Sieverts' apparatus releases the gas in small amounts, thus leaving to the sample at least 6 s between one step and another to react and stabilize, while a continuous flow of gas does not allow any settling or relaxation of temperatures and stresses. As a matter of fact, the kinetics of hydrogen release is approximately an order of magnitude slower for a number of pellets in the reactor rather than for a single pellet in the sample holder of the Sieverts' apparatus.

Both absorption and desorption graphs display a first part where almost 1 wt.% of hydrogen is shown to react: this is mostly due to the shape of the flow profiles of Fig. 3c, where the initial sudden hydrogen flow, due to the 8 bar pressure, is limited by the controller

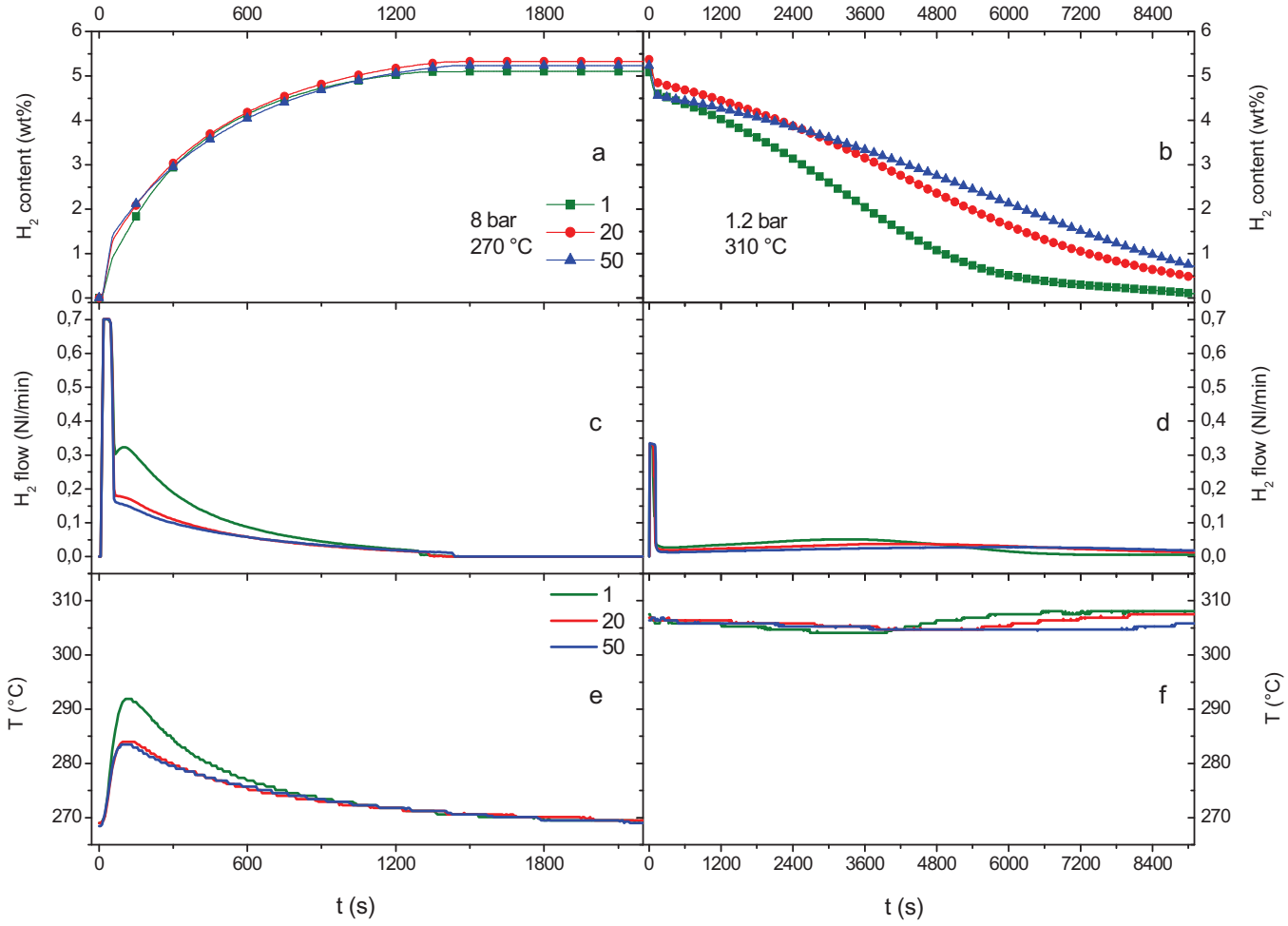

Fig. 3. Absorption (a, c, e) and desorption (b, d, f) data vs. time for first, intermediate and last hydrogen a/d cycles. Hydrogen content plots (a and b) were obtained from flow data (c and d) retrieved from instruments during the test. Temperatures (e and f) were those registered in the central part of the reactor.

and then the valve is fully opened. Fig. 3d represents the flows during hydrogen release, where the minimum useful pressure of 1.2 bar limits the flow to lower values and causes slow desorption kinetics: in fact the first flow peak does not reach the value of 0.7 Nl/min (instrumental limit) and the subsequent decrease of flow is more rapid than in Fig. 3c.

The Fig. 3e and f display the temperatures registered by the central thermocouple (clearly visible in the radiography) placed inside the reactor. Most significantly, Fig. 3e shows how temperature increases suddenly with the exothermic hydrogen absorption, but just a maximum difference of about 20 °C was detected between the central part of the reactor and the sides. The thermocouples placed at the extremity of the reactor registered only small variations in temperature (and so not reported in the figure), because they were in contact with just one pellet and in a position of higher heat dispersion: the central thermocouple was more affected by the contact with the pellets and, moreover, the steel pipe could disperse heat less easily than at the sides. This was a really localized effect, in fact the oil temperature was not affected appreciably and the heat flow was below 65 W for absorption. In contrast, previously developed reactors containing a comparable amount of powder were suffering of almost 80 °C of local over-heating (Fig. 11 in ref. [2]). The data for hydrogen a/d in a larger reactor containing not previously compressed hydride powder show both a decrease in kinetics (the time for complete reaction is doubled) and in storage capacity which drops from 5.5 wt.% to 3 wt.% (Fig. 9 in ref. [2]).

In the release process of the present experiment the slow kinetics allows the material to complete the endothermic reaction without a significant change in temperature: a loss of few degrees of temperature was detected only by the central thermocouple.

The radiographic picture of Fig. 4a shows the ordered disposition of the pellets assembled inside the reactor and how they are

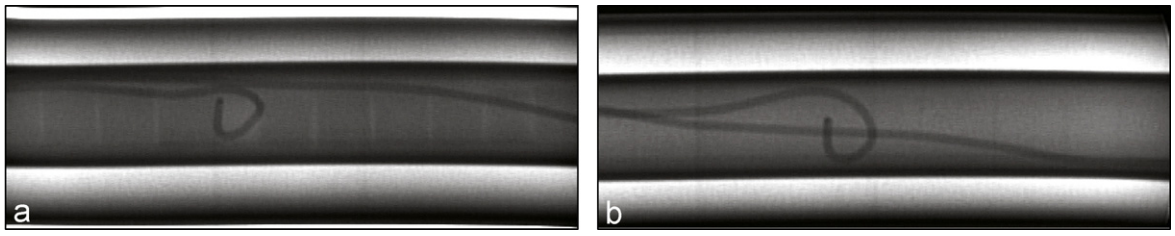

Fig. 4. Radiographies of the central part of reactor before (a) and after (b) 50 hydrogen a/d cycles.

separated by the carbon mat; darker zones correspond to denser material, the pellets, while a lighter shade of grey corresponds to carbon mat. The same central zone of the reactor, examined after 50 cycles and reported in Fig. 4b, shows a reversed contrast between pellets and carbon mat regions and a considerable decrease of the interspaces thickness. The reason for this is twofold: the increase of the volume of pellets after cycling and migration of part of the metallic component of the pellets to their surface. This agrees with previous observations on the behaviour under cycling of single pellets [3]. It is easy to foresee that the behaviour of the system might be significantly improved with wider interspaces between pellets inside the reactor filled with a light good heat conductor, as the carbon fibres used in the present case.

4. Conclusions

This work was carried out to evaluate the scaling up performances of a MgH_2-based composite material pressed in form of cylindrical pellets. The hydrogen a/d tests, performed on a reactor containing a number of pellets, behave differently from previous experiments on a single pellet: slightly lower gravimetric capacity and worse desorption kinetics. Nevertheless, the use of pellets in a reactor (well separated e.g. by carbon-fibre mat) instead of a powder bed, facilitates the heat exchange and avoids local overheating and subsequent detrimental strong compaction of the powder which has been seen in previous experiments to lead to rapid degradation of performances.

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