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Tests on mechanically alloyed Mg_2Ni for hydrogen storage

P. Muthukumar [a], M. Prakash Maiya [a], S. Srinivasa Murthy [a], R. Vijay [b,*], R. Sundaresan [b]

[a] *Refrigeration and Air Conditioning Laboratory, Department of Mechanical Engineering, Indian Institute of Technology Madras, Chennai 600036, India*

[b] *International Advanced Research Centre for Powder Metallurgy and New Materials, Balapur, Hyderabad 500005, India*

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Abstract

Mg_2Ni alloy was prepared by mechanical milling followed by annealing at 480 °C under argon atmosphere. The alloy was tested for hydrogen absorption/desorption characteristics on a small sample of 5 g in a laboratory equipment, and for storage properties on a large sample of 375 g in a reactor. Kinetics studies on the small sample showed the same fast absorption at 250–330 °C under 30 bar pressure, and complete desorption at 300–330 °C. Studies were carried out in the temperature range of 200–300 °C with a supply pressure up to 20 bar in the storage device. The large sample showed increase in both absorption rate and storage capacity with supply pressure. However, while storage capacity increased with increase in initial bed temperature, average absorption rate decreased with increase in temperature. At a given bed temperature, absorption kinetics were significantly faster than the desorption kinetics. Maximum hydrogen storage capacity of 3.67 wt%, close to the theoretical limit, was observed in the reactor at a supply pressure of 20 bar and initial bed temperature of 300 °C. The hydrogen storage capacity of the larger mass in the reactor was comparable to the smaller sample mass.

Keywords: Mechanical milling; Absorption/desorption kinetics; Pressure–composition isotherm (PCI); Hydrogen storage device

1. Introduction

It is well established that certain intermetallic compounds exhibit good potential for storing hydrogen as they absorb and desorb hydrogen at favorable pressures and temperatures. Magnesium–nickel alloys based on Mg_2Ni, which can be synthesized by both melting and mechanical milling routes, can have hydrogen storage capacity as high as 6 wt% [1].

Although magnesium hydride has a high hydrogen content (7.6 wt%) it has not been considered for hydrogen storage because of its slow kinetics and high temperature of absorption and desorption. There have been reports on Mg-based composites and alloys for hydrogen storage. Liang et al. [2] prepared Mg–35 wt% $FeTi_{1.2}$ hydrogen storage materials by mechanical milling of mixed elemental magnesium and $FeTi_{1.2}$ alloy powders. Their results showed that the P–C–T characteristics, hysteresis, plateau pressure, storage capacity, and hydriding and dehydriding rates changed substantially with milling time. Mechanical milling produced fine powder with nano-sized grains, which led to increase in the hydriding and dehydriding rates. The hydrogen storage capacity had a maximum value of 2.7 wt% for powder subjected to 7 h of milling, and further increase in milling time caused a reduction in storage capacity. Friedlmeier and Groll [1] presented an experimental investigation of the hydrogen absorption rate of Ni-doped Mg powders. The hydriding behaviour of Mg(Ni) and Mg showed a complex dependence on pressure and temperature, with the catalytic effect of Ni on $Mg–H_2$ reaction being strong at temperatures below 300 °C. Dehouche et al. [3] studied the hydriding–dehydriding properties in terms of long-term cyclic stability as well as thermal stability of nano-structured MgH_2 with 0.2 mol% Cr_2O_3 addition. Stable absorption kinetics was observed for at least 17 cycles at 350 °C and for at least 1000 cycles at 300 °C, while desorption kinetics slowed down by a factor of four after 1000 cycles at 300 °C. During the cycling the maximum hydrogen absorption increased slightly from 5.9 to 6.4 wt%. Reiser et al. [4] investigated Mg-based alloys for hydrogen storage as well as for thermal storage applications over a range of 250–550 °C. Among these alloys, $Mg/MgH_2 + 2$ wt% Ni had the highest H_2 storage capacity of about 6 wt%. Vijay et al. [5] evaluated Mg_2Ni-based alloys (Mg_2Ni, $Mg–Mg_2Ni$ and $Mg_2Ni–Ni$) prepared by mechanical alloying followed by

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* Corresponding author. Tel.: +91 40 24441075; fax: +91 40 24442699.
E-mail address: vijay@arci.res.in (R. Vijay).

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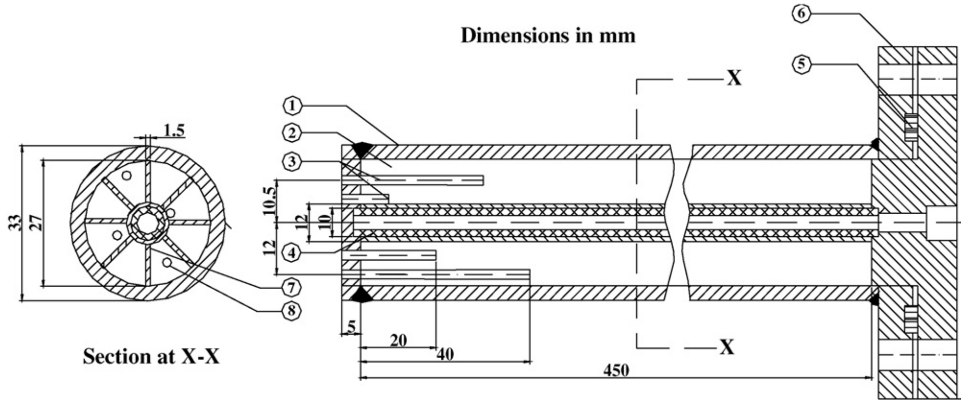

Fig. 1. Schematic of annular cylindrical reactor. (1) Reactor wall; (2) metal hydride; (3) thermocouple; (4) filter; (5) Teflon washer; (6) flange (not to scale); (7) copper fin (eight numbers, 1.5 mm thick); (8) thermocouple location.

annealing. The maximum absorption of hydrogen was close to the theoretical limit in stoichiometric and superstoichiometric compositions in the temperature range 250–330 °C, with complete desorption at 300–330 °C.

In general, most of the reported works aim to generate the pressure–composition characteristics in the form of isotherms (PCI) and kinetics based on small alloy samples under controlled laboratory conditions. The performance of practical storage systems depends on the reactor configuration and the heat and mass transfer in the hydride bed. In this present study, the hydrogen storage material Mg_2Ni was tested on large samples in a storage device at various supply pressures and operating temperatures.

2. Experimental

2.1. Alloy preparation

Blended powders of different compositions of magnesium (purity 99.7%, average particle size of 250 μm) and nickel (purity 99.8%, average particle size of 3 μm) to form stoichiometric Mg_2Ni were subjected to ball milling in an attritor using 6 mm stainless steel balls. The ball to powder ratio maintained during milling was 15:1. Milling was carried out for 8 h under argon cover and the quantity of powder used for each run was 850 g. Loading and unloading of powders were carried out in an argon atmosphere. The powder after 8 h of milling was granular and was subjected to annealing at 480 °C under argon atmosphere for 1 h. The powders were characterized for identification of phase content before and after annealing by X-ray diffraction in a Brukers XRD machine using Cu Kα radiation.

2.2. Hydrogen storage studies

The hydrogen absorption/desorption characteristics of the powders were measured on small samples by volumetric principle using a unit similar to the one reported by Friedlmeir et al. [6]. Studies were carried out on sample size of 5 g. A constant hydrogen flow of 1.5 ml/min and constant hydrogen pressure was maintained during PCI and absorption/desorption kinetics measurements, respectively. The data was recorded continuously throughout the experiments.

2.3. Hydrogen storage device

The metal hydride reactor employed for studies at larger scale was of annular cylindrical configuration as shown in Fig. 1. The reactor was made of stainless steel (SS-316) tube of 3 mm wall thickness and the filter was of sintered SS-316 of 2 μm pore size. Copper fins (1.5 mm thick) were inserted to enhance the effective thermal conductivity of the hydride bed. One end of the reactor was closed with a brazed assembly of four grounded metal-sheathed K type thermocouples (sensitivity 0.1 °C) while the other end of the reactor was flanged. A thermostatically controlled high temperature oven was used for heating the reactor, while cooling was done by rejecting heat to the ambient. Other instrumentation and sensors are shown in Fig. 2. Piezo resistive type pressure transducers (sensitivity 0.01 bar) of range 0–100 bar were used for measuring the reaction pressure (P_1) and the supply pressure (P_2). A Coriolis mass flow meter (sensitivity 0.001 g) was used for measuring the hydrogen flow rate, total flow and temperature of the H_2 gas. High-pressure packless bellow valves were used in the gas line for controlling/diverting the gas flow.

Mg_2Ni alloy (375 g) was filled in the annulus between the tube and the filter. The activation of annealed Mg_2Ni was carried out at 250 °C under hydrogen at 20 bar supply pressure. The reactor was evacuated down to 10^{-3} mbar, and back filled with hydrogen, flushing three times by evacuation and refilling. Subsequently with the reactor maintained at 250 °C, hydrogen at 20 bar pressure was allowed into the reactor and the mass flow was monitored. During the first cycle of operation, about 0.47 wt% of hydrogen absorption was obtained in 20 min. Then the reactor was heated to 300 °C and the hydrogen was desorbed. During the consecutive absorption/desorption cycles increasing hydrogen absorption was observed and stabilized at a maximum storage capacity of 3.67 wt% after 15 cycles.

After the activation as above, the reactor was heated to the preset value of the absorption temperature in a high temperature oven, and was taken outside during absorption measurements. Valves V_1 to V_4 were opened (V_5 and V_6 closed), and hydrogen was allowed to flow into the reactor at a preset supply pressure in the range 5–35 bar using a pressure-reducing valve. The temperature of reactor was maintained by utilizing the heat of absorption during the absorption process. Exothermic absorption of hydrogen was continued till the process was completed, as indicated by zero flow on the mass flow meter. Then the charged reactor was brought to the ambient temperature. For desorption the reactor was heated to above 300 °C causing the equilibrium pressure of the hydride to increase. Valves V_1, V_2 and V_6 were opened to release the hydrogen.

3. Results and discussion

The XRD patterns of the 8 h milled powder before and after annealing are shown in Fig. 3. The powder shows elemental Mg and Ni peaks without the formation of Mg_2Ni phase. But the annealing completely transformed this into Mg_2Ni phase without any noticeable residual Mg and Ni phases. One hour of annealing was sufficient to get the complete formation of Mg_2Ni phase.

The hydrogen storage properties discussed below were measured on a sample mass of 5 g. Fig. 4 shows the PCI for absorption and desorption of hydrogen by Mg_2Ni alloy at 250, 300 and 330 °C. The absorption and desorption plateaus are

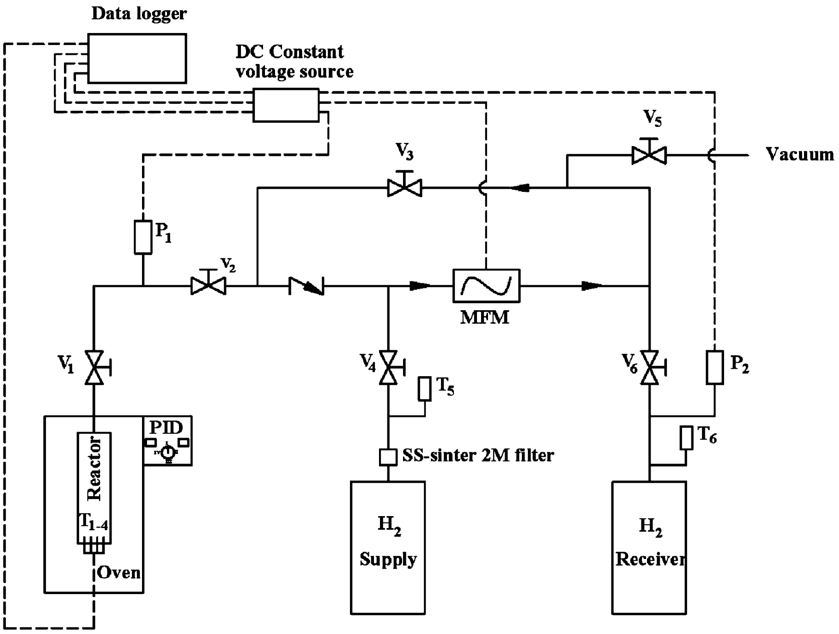

Fig. 2. Test setup for hydrogen storage device fir Mg-based alloys. MFM: mass flow meter; P: pressure transducer; T: thermocouple; PID: PID controller; (⋈) packless bellow sealed valves; (↘) one way valve; (—) gas line; (- - -) electrical wiring.

inclined confirming reported observations [7]. The absorption plateau begins at 2 bar for 250 °C, 4 bar for 300 °C and 6 bar for 330 °C. The absorption plateau at 300 °C and desorption plateau at 330 °C overlap in their respective hydrogen content range. Hydrogen desorption was nearly complete at about 1 bar at 300 and 330 °C, but the desorption plateau was below 1 bar at 250 °C. The alloy absorbed 3.4 wt% (95% theoretical) at all the temperatures.

The absorption kinetics of Mg_2Ni alloy at 250, 300 and 330 °C are shown in Fig. 5. The alloy exhibited fast kinetics at all the temperatures studied and reached the 90% of theoretical capacity in 200 s. On the contrary, the alloy exhibited quite different desorption kinetics at different temperatures. Fig. 6 indicates that unlike the absorption kinetics, the desorption kinetics is slower and the rate of desorption decreases with temperature. The alloy took 60 and 300 s to desorb 90% of the absorbed hydrogen at 330 and 300 °C, respectively. The des-

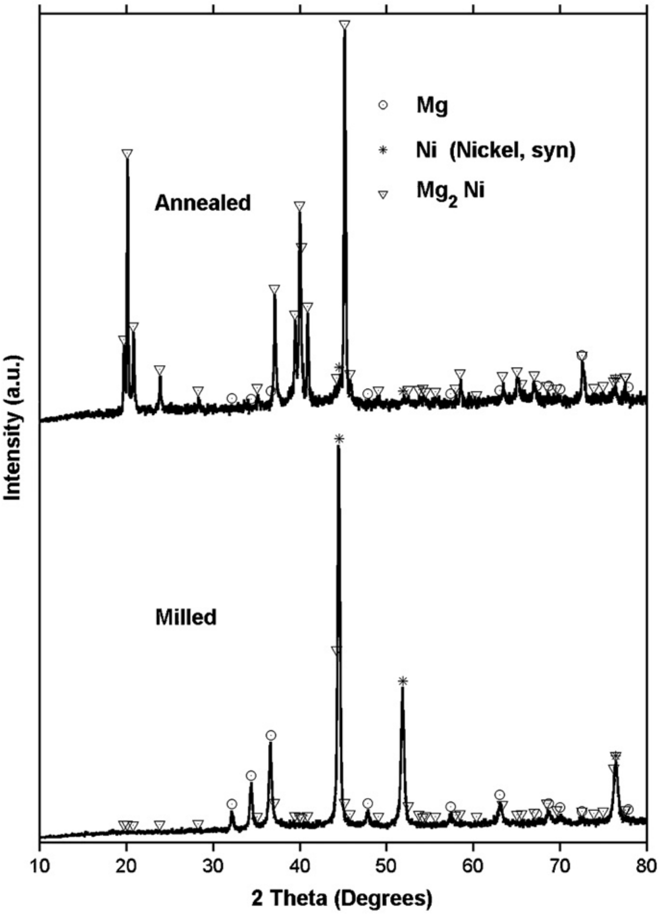

Fig. 3. XRD of Mg_2Ni milled for 12 h (dry) and subsequently annealed at 480 °C.

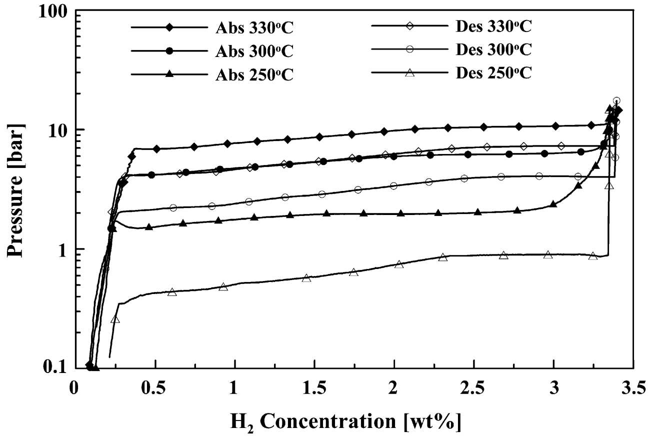

Fig. 4. PCI of Mg_2Ni at different temperatures.

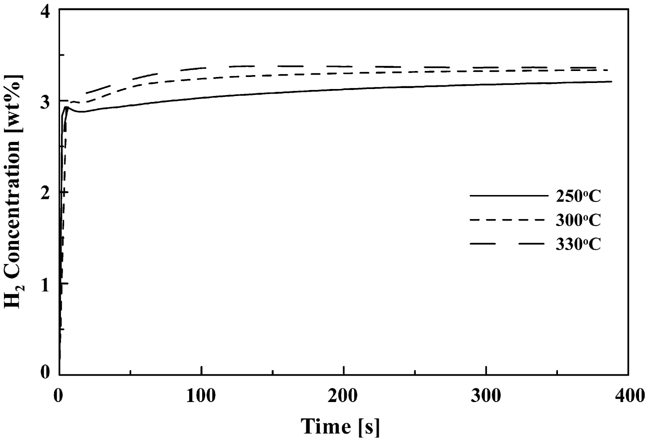

Fig. 5. Absorption kinetics of Mg_2Ni alloy under 30 bar pressure.

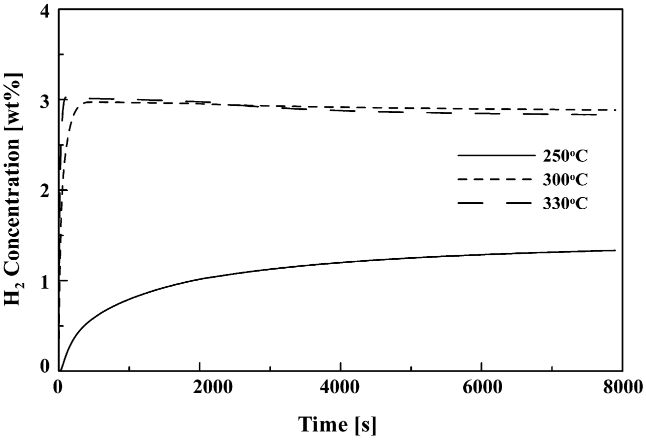

Fig. 6. Desorption kinetics of Mg_2Ni alloy under 1 bar pressure.

orption rate was much slower at 250 °C and only 25% of the absorbed hydrogen could be desorbed in 40 min. In addition to the slow desorption kinetics, the desorption plateau pressures were below 1 bar at 250 °C. Therefore, even though absorption of hydrogen has been reported even at lower temperatures [8], study of kinetics was not considered relevant for temperatures below 250 °C.

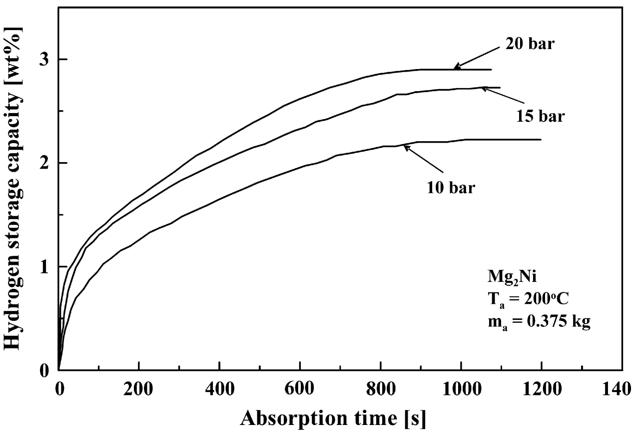

Fig. 7. Effect of supply pressure on reactor performance.

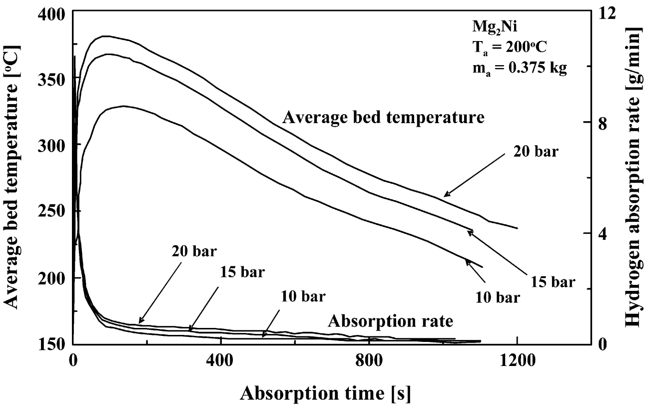

Fig. 8. Effect of supply pressure on hydrogen absorption rate and average reactor temperature at 200 °C.

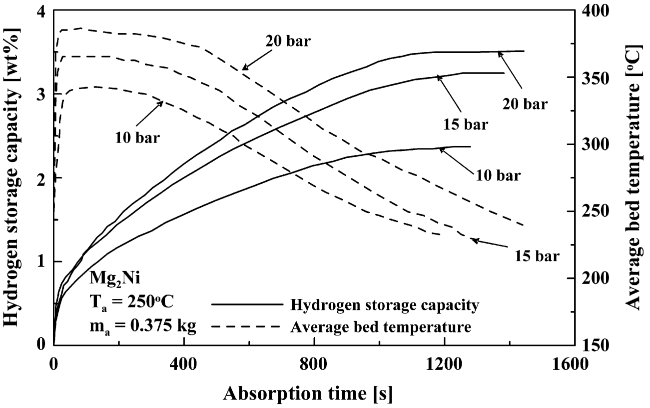

Fig. 9. Effect of supply pressure on hydrogen absorption rate and average reactor temperature 250 °C.

With the larger sample size studied in the storage device, the initial bed temperature and supply pressures were varied from 200 to 300 °C, in steps of 50 °C and 10–20 bar in steps of 5 bar, respectively. Fig. 7 shows that at higher supply pressure the hydrogen storage capacity increases due to increase of driving potential. However, the increase of storage capacity is not significant above the supply pressure of 15 bar. The reactor temperature also increases sharply from the initial value of 200 °C to

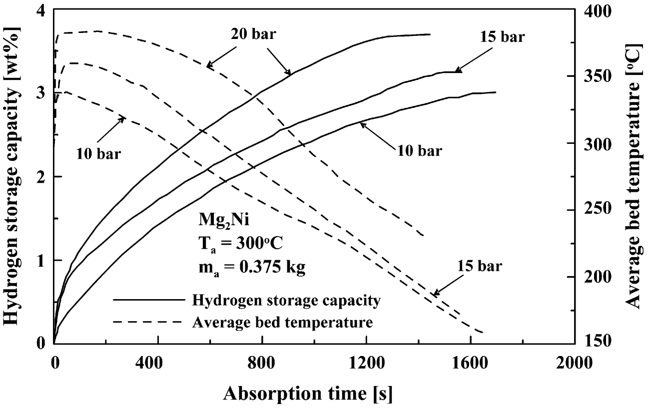

Fig. 10. Effect of supply pressure on hydrogen absorption rate and average reactor temperature 300 °C.

about 370 °C and then decreases gradually to the initial absorption temperature, which is illustrated in Fig. 8. It may be noted that heat is supplied initially only for raising the bed temperature from ambient to the preset value of absorption temperature (200 °C). During the absorption process the bed temperature remains above 200 °C due to the heat of absorption. For any given supply pressure, the absorption rate is found to be significantly smaller compared to that seen in Fig. 5. This is due to heat transfer resistance of the hydride reactor, which causes an increase of the reactor temperature and consequently the hydride equilibrium pressure, leading to a lower driving potential for hydrogen transfer and correspondingly slower absorption kinetics. It may also be noted that the rise of mean bed temperature is higher at higher supply pressure due to faster absorption of hydrogen, i.e. the heat generation rate is higher at higher supply pressure. An optimised reactor design should be capable of transferring the absorption heat at fast rate with minimum rise in reactor temperature. The overall reactor heat transfer coefficient (which combines the effects of convective resistance at the reactor outer wall, the contact resistance at the reactor inner wall and the conductive resistance of the reactor itself) plays a major role in controlling the absorption rate. One means to improve the heat transfer inside the reactor is to provide suitable fins, as has been done in the investigated reactor.

Fig. 8 also illustrates that the absorption rate increases steeply in the initial period due to the sudden peak absorption kinetics (higher driving potential), and falls immediately after reaching the peak and then decreases gradually reaching zero at the end of the absorption process. It can be noted that the absorption rates are nearly uniform initially, then increase marginally with higher supply pressure and tend to zero at the end of the absorption process.

Unlike many hydriding alloys [9], Mg_2Ni stores more hydrogen at higher initial bed temperatures. This behaviour is seen from Figs. 9 and 10. However, the effect of initial absorption temperature on average bed temperature is not significant, as it varies only with respect to the supply pressure. The maximum storage capacity of 3.67 wt% was achieved for the initial absorption temperature of 300 °C and the supply pressure of 20 bar. In

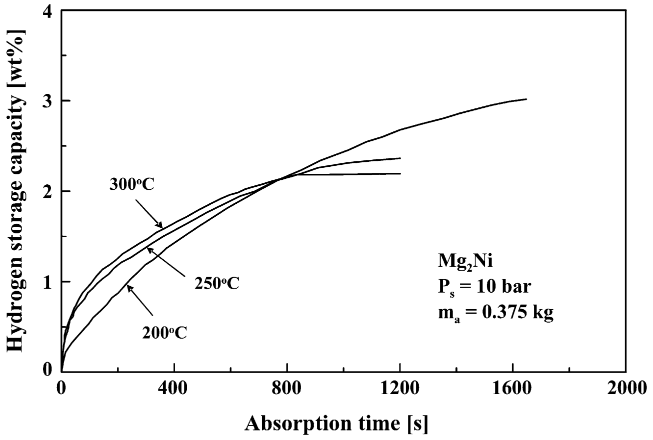

Fig. 11. Effect of initial bed temperature on hydrogen storage capacity at supply pressure of 10 bar.

Table 1
Saturation absorption capacity and average absorption rate of Mg_2Ni alloy

Temperature (°C)	10 bar			20 bar			30 bar		
	Time (s)	Absorption capacity (wt%)	Average absorption rate (wt%/s)	Time (s)	Absorption capacity (wt%)	Average absorption rate (wt%/s)	Time (s)	Absorption capacity (wt%)	Average absorption rate (wt%/s)
200	890	2.19	0.0025	885	2.68	0.0030	830	2.88	0.0035
250	1118	2.36	0.0021	1260	3.24	0.0026	1159	3.50	0.0030
300	1643	3.02	0.0018	1510	3.24	0.0021	1280	3.67	0.0029

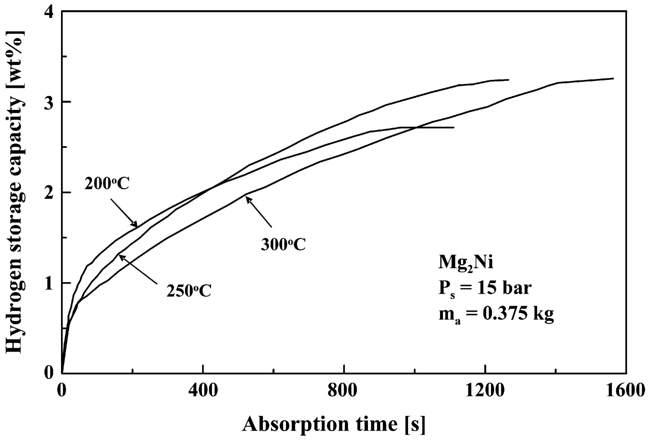

Fig. 12. Effect of initial bed temperature on hydrogen storage capacity at supply pressure of 15 bar.

this regard both the behaviour of the large batches of the alloy in the reactor was comparable to that of the small samples.

It is well known that Mg_2Ni absorbs hydrogen effectively above 230 °C [4]. However, in the lower temperature range of 200–250 °C, the heat released during the initial hydrogen absorption by the material causes the reactor temperature to increase to above 250 °C. This would enhance the absorption rate thereby promoting further hydride formation. Hydrogen concentration in the alloy and reactor temperature increase with time. After about 200 s, hydrogen absorption rate decreases due to higher reactor temperature (lower driving potential) and becomes flat at the end of absorption process. Figs. 11–13 show that the hydrogen storage capacity of the alloy in the reactor as functions of supply pressure and initial absorption temperature. The saturation absorption capacity and average absorption rate at each temperature and pressure are given in Table 1. Although, the saturation absorption capacity increased with initial absorption temperature, the average absorption rate decreased with increase in initial absorption temperature. The high absorption rate at low initial bed temperature is due to higher driving potential. However, at high initial reactor temperature the hydride temperature remains above 230 °C, which helps to retain the alloy in absorbing mode further increasing the hydrogen storage capacity. From these observations it may be concluded that the hydride demands minimum of 230 °C for completion of absorption process.

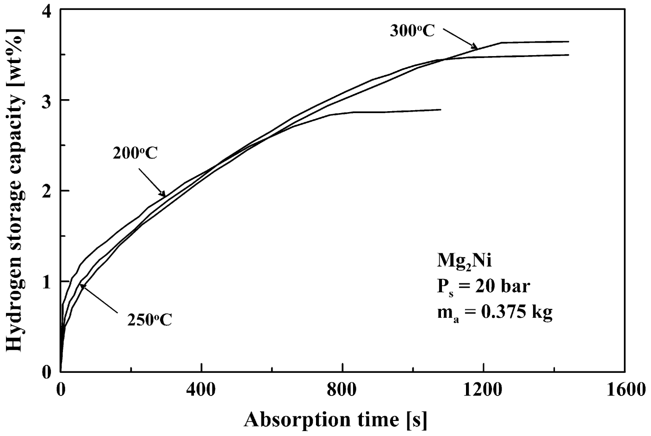

Fig. 13. Effect of initial bed temperature on hydrogen storage capacity at supply pressure of 20 bar.

4. Conclusions

Mg_2Ni alloy was prepared by mechanical milling followed by annealing at 480 °C under argon atmosphere. Hydrogen storage properties of the alloy was evaluated at 250, 300 and 330 °C on a sample mass of 5 g. The PCI showed inclined plateaus with the plateau pressure and the plateau slope increasing with temperature. The alloy powder exhibited faster absorption kinetics than the desorption kinetics at corresponding temperatures. Storage tests in a reactor containing 375 g of Mg_2Ni revealed that the hydrogen storage capacity and absorption rate increased with supply pressure. The average absorption rate decreased with increase in initial absorption temperature. A maximum storage capacity of 3.67 wt% equivalent to its theoretical capacity could be achieved for an initial absorption temperature of 300 °C and supply pressure of 20 bar. The absorption behaviour of large mass of Mg_2Ni alloy was similar to that of the smaller sample mass.

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