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DESIGN AND DEVELOPMENT OF HYDROGEN ABSORPTION/DESORPTION HIGH PRESSURE APPARATUS BASED ON THE PRESSURE REDUCTION METHOD

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Abstract—A high-pressure apparatus for the measurement of hydrogen absorption/desorption characteristics, such as reversible hydrogen intake capacity, kinetics, plateau pressure, hysteresis and plateau slope of alloys and intermetallic compounds in the ranges $0.002 \leqslant P/\text{bar} \leqslant 100$ and $300 \leqslant T/\text{K} \leqslant 673$, based on the pressure reduction method, is described. Special stainless steel tubes, adapters, tees, valves and pressure heads are used to develop the measuring system, while the hydrogen reaction chamber is constructed using special stainless tube and copper block. This apparatus is also capable of being used as it stands for the study of the kinetics of absorption, as well as of the hydrogen decrepitation route in the powder metallurgical production of magnetic alloys. The satisfactory performance of the apparatus is checked with the hydrogen absorption isotherms in palladium. © 1998 International Association for Hydrogen Energy

NOMENCLATURE

$r = n_\text{H}/n_\text{M}$	number of hydrogen atoms per metal atom
m	mass of the sample
M	molecular weight of the sample
R	gas constant
P_E	hydrogen equilibrium pressure
P_A	hydrogen initial pressure
V_S	volume of the reaction cell
V_C	volume of the connecting tubes
V_A ($V_{\text{C,2}} + V_\text{A}$), $V_{\text{C,1}}$	volumes of the measuring parts

INTRODUCTION

A rapid development in the field of metal hydrides has been noticed in the recent years because of their potential as a hydrogen storage medium. Hydrogen storage and application devices such as hydrogen engines, refrigeration or heat pumps, metal hydrogen batteries, thermodynamic machines and vacuum getters are of great interest because they offer pollution-free operation. After

several decades of effort, the full appreciation of the potential of metal hydrides as a storage medium for future fuel came in the discovery of a series of alloys such as LaNi$_5$ (MmNi$_5$), MgNi$_2$ and TiFe [1, 2]. However, these alloy systems have several disadvantages, and hence the efforts to develop new metal hydrides with specific applications in mind are in progress. The strategy is to optimize first the alloy composition for excellent hydrogen absorption–desorption properties, such as large reversible hydrogen intake capacity, rapid kinetics, favourable plateau pressure at optimum temperature depending on the application, minimum hysteresis with nearly zero plateau slope and minimum decrepitation, and then pave the way for a metal hydride reactor with a large quantity of materials. Besides, the hydrogen decrepitation process combined with milling is now established as an integral part in the production of Nd–Fe–B permanent magnets [3–5]. In this process, the cast Nd–Fe–B type alloy is readily broken into a relatively fine powder by hydrogen absorption–desorption cycles. The hydrogen decrepitation process is now established as an integral part of the production of giant magnetostrictive REFe$_2$ alloys [6, 7]. Besides, the nitrogenation of Fe magnetic materials such as RE$_2$Fe$_{17}$ and REFe$_{12}$ improves the magnetic properties drastically and efforts are devoted to develop promising permanent magnets [8, 9]. The present apparatus is designed for the study of the hydrogen absorption–desorption isotherms and the study of the

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hydrogen reversible intake capacity, kinetics, plateau pressure, hysteresis and plateau slope of alloys and intermetallic compounds, as well as for the production of Nd–Fe–B permanent magnets, giant magnetostrictive $REFe_2$ alloys using hydrogen decrepitation process, and for the nitrogenation of RE_2Fe_{17} and $REFe_{12}$ magnet materials.

EXPERIMENTAL FACILITY

The high-pressure absorption–desorption experimental apparatus based on the pressure reduction method consists of two parts; the measuring chamber and reactor chamber.

Measuring chamber

The hydrogen concentration dissolved in the alloy is measured using the measuring part (Fig. 1) which has been fabricated using special stainless tubes, adapters, valves, and tees procured from Nova (Switzerland) which can withstand up to 4000 bar. The volumes $V_{C,1}$ and $V_{C,2}$,

approximately 500 cc and 100 cc respectively, are fabricated using high-quality stainless steel. The entire stainless tube portion is wrapped with thin plastic tubes through which water from a thermostat (20°C) is circulated. In addition, the entire unit is insulated with glass wool. The pressure of hydrogen in the range 0.002–2 bar is measured using pressure head GH_2 along with a sophisticated measuring system (calibrated in Torr) which will allow us to measure the dissolved hydrogen concentration in the alloy very accurately; the amount of dissolved gas in the range 1–100 bar (or 1–50 bar) is measured using pressure head GH_1 and a measuring system procured from Burster (Germany). The entire measuring part is fixed in a box which can be carried to the place where the reaction chamber is located. Figure 2 shows the photograph of the developed measuring chamber as per the specification given in Fig. 1.

Reactor chamber

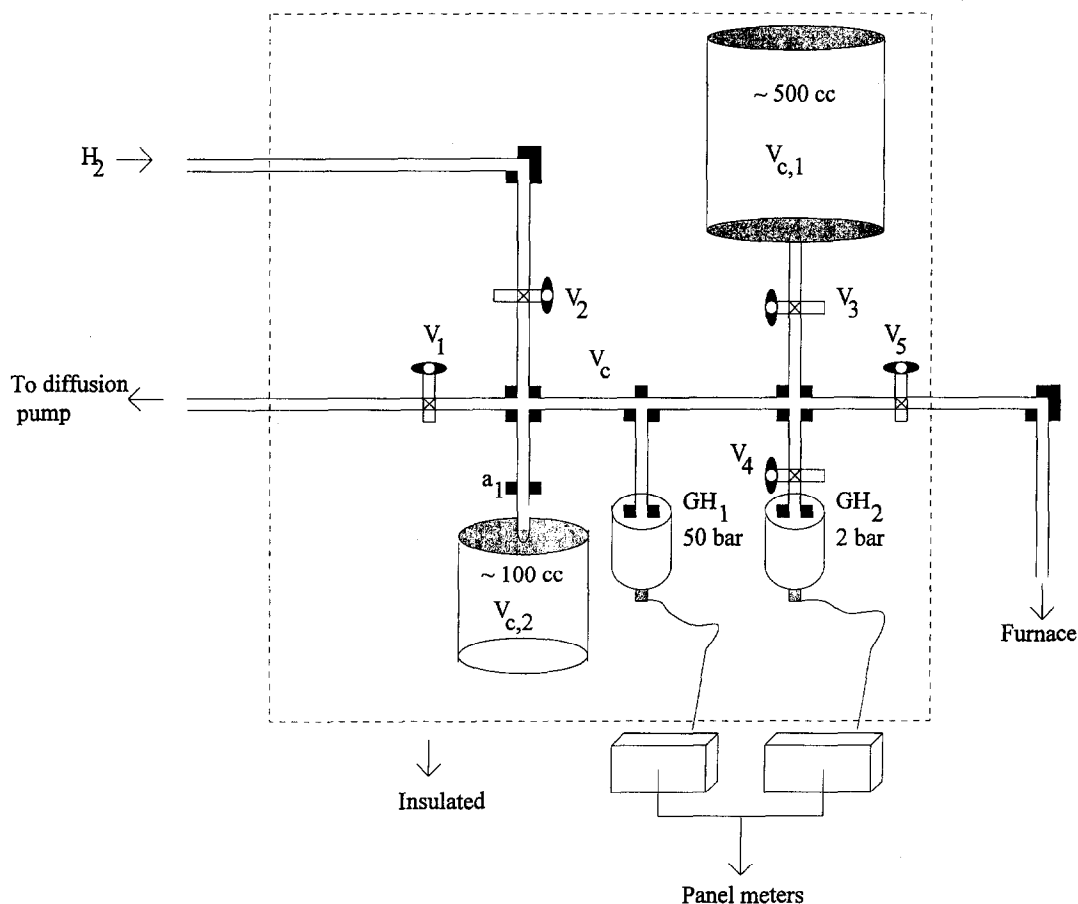The reactor chamber, where the gas is allowed to interact with the alloy, consists of a sample cell and a furnace.

Fig. 1. Schematic diagram of measuring chamber of the high-pressure absorption–desorption facility developed using the pressure reduction method.
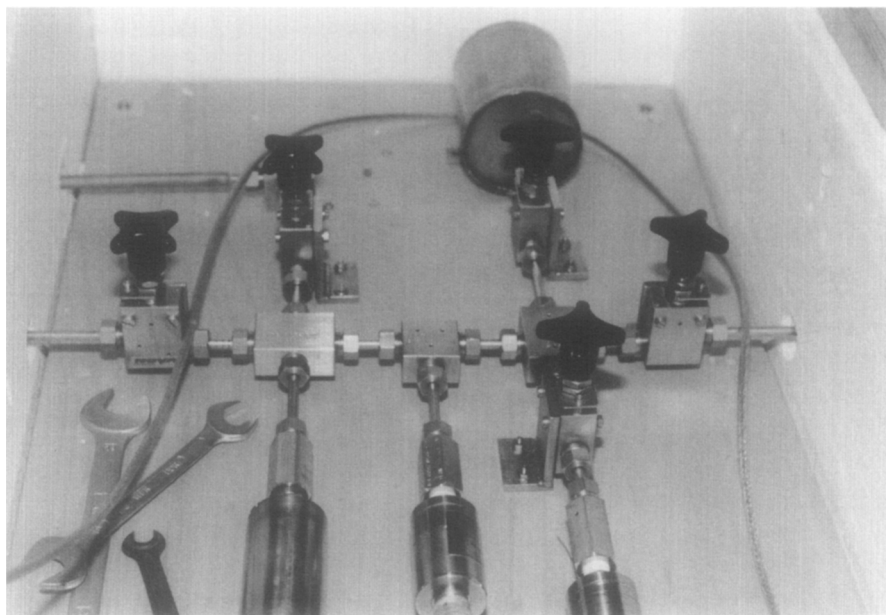
Fig. 2. Photograph showing the measuring chamber of the high-pressure absorption–desorption facility.

The sample cell consists of a special stainless steel tube of outer diameter 10 mm, inner diameter 8 mm and length 150 mm in which the molybdenum sample crucible is placed. Since copper has excellent thermal conductivity, the stainless tube is placed in a cylindrical copper block of diameter 20 mm and length 170 mm by drilling a hole of diameter 10 mm and length 150 mm (Fig. 3). This will further improve the safety during operation. The entire sample cell is then connected to the measuring chamber using a gasket. The gasket is protected from the furnace heat by circulating water from the thermostat (20°C) in the lower flange. Any diffusion of hydrogen at high pressure and temperature can be eliminated by gold coating the inner surface of the cell, as the hydrogen absorption of gold is $r = n_H/n_M = 1.0 \times 10^{-6}$ at 873 K and 1 atm [10]. The cell is kept inside a resistance furnace whose temperature can be maintained with an accuracy of $\pm 0.5°C$ for the range $300 \leqslant T/K \leqslant 673$. The temperature of the sample is measured by inserting a chromel–alumel thermocouple into the cylindrical copper block by drilling a hole close to the stainless tube (Fig. 3).

Calibration of the measuring part

The volumes $V_{C,1}$ and $V_{C,2}$ are obtained by disconnecting $V_{C,1}$ (along with the stainless tube up to valve v_3) and $V_{C,2}$ (along with the stainless tube up to adapter a_1) and weigh them with and without toluene whose density is known. After fixing them again, the entire unit is evacuated to 10^{-6} Torr by using a diffusion pump and liquid N_2 trap. At this situation, only valve v_2 is closed and the rest of the valves are opened. After closing v_5 and v_1, a measured quantity of hydrogen is admitted into volume $V_{C,1}$ and the volume of the connecting tubes V_c

by opening v_2 with pressure p_1 (measured using GH_2 for less than 2 bar; otherwise using GH_1). v_4 is always closed when the system pressure is more than 2 bar. Now v_3 and v_2 are closed and the entire system is evacuated to 10^{-6} Torr by opening v_1. After closing v_1 (v_1, v_2, v_3 and v_5 are closed and also v_4 if the pressure is > 2 bar), v_3 is opened; from the drop in the pressure, the volume of the connecting tubes V_c is calculated. This is repeated for different pressures, taking account of van der Waal's corrections for hydrogen at high pressures, and the average value of V_c is found. In order to find out the volume of the reaction cell, the entire system is evacuated after closing v_2 and v_3. After closing v_5 and v_1, a measured quantity of hydrogen is admitted to V_A ($= V_{C,2} + V_c$). From the drop in the pressure after opening v_5, the reaction volume V_S at different reaction temperatures is found out taking care of the thermal expansion of hydrogen gas. The typical values of the volumes used in the present set-up are $V_A = V_{C,2} + V_c = 100.2 + 8.7$ cc; $V_{C,1} = 488.6$ cc; $V_S = 20.6$ cc (300 K) to 15.5 cc (673 K).

Determination of absorption, desorption isotherms and kinetics of absorption

The composition–temperature–pressure absorption relation in any alloy can be determined in the ranges $0.002 \leqslant P/\text{bar} \leqslant 100$ and $300 \leqslant T/K \leqslant 673$ using the following procedure: m grams (2–3 g) of the sample with molecular weight M is enclosed in a Mo crucible and inserted in the reaction cell which in turn is connected to the charging system. Prior to an absorption run, the whole system is evacuated to $P/\text{bar} < 7 \times 10^{-9}$ and the sample is degassed at 723 K for 1–2 h. Thereafter the sample is activated for absorption of hydrogen by charg-
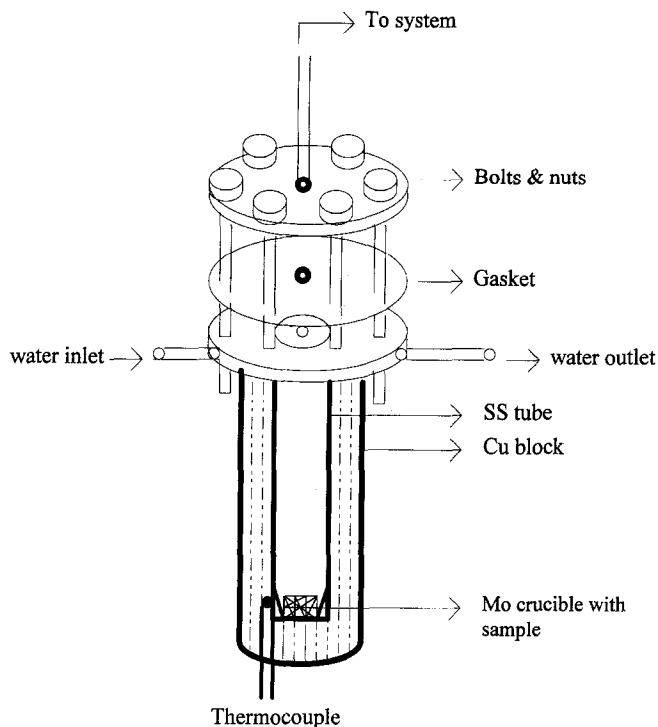
To system

Bolts & nuts

Gasket

water inlet → ← water outlet

SS tube
Cu block

Mo crucible with
sample

Thermocouple

Fig. 3. Schematic diagram of the reaction chamber of the high-pressure absorption–desorption facility.

ing it with hydrogen of purity 99.9999% (P/bar = 50; T/K = 673 K; t/h = 2), decharging it and then slowly cooling down to room temperature. In this way, a fresh surface is produced for quantitative and rapid measurements of hydrogen absorption. After degassing the sample at 723 K, the sample is cooled to the desired temperature at P/bar $< 7 \times 10^{-9}$. A measured quantity of hydrogen with initial pressure P_A is introduced in V_A ($V_{C,1}$ is used if the sample absorbs a large amount of hydrogen) and then allowed to contact with the sample by opening the valve v_5. When equilibrium between gaseous H_2 and absorbed H is established (P_E), as judged from the reading of pressure as a function of temperature, the sample is cooled to the next desired temperature and a new equilibrium pressure is established. This procedure is continued in steps down to the lower temperature limit, T/K = 300 K. The sample is again degassed at 723 K and a new run started with an initial pressure different from the foregoing one. The hydrogen concentration in the sample at the equilibrium pressure P_E is calculated from initial pressure P_A and the pressure drop during the absorption reaction at constant and calibrated volume and constant temperature using

$$r = \frac{n_H}{n_M} = 2M \left\{ \frac{P_A V_A - P_E (V_A + V_S)}{mRT} \right\} \quad (1)$$

where R is the gas constant and T is the room temperature. The equilibrium points in the isotherms at high

pressures can also be easily obtained by the step-up method. In this method, after equilibrium pressure P_E is established at any particular temperate, v_5 is closed and an additional measured quantity of hydrogen (pressure P'_A) is allowed into V_A by opening v_2. Valve v_5 is then opened and the final equilibrium pressure P'_E is established and the amount of hydrogen dissolved at the equilibrium pressure $P_{E'}$ is obtained by

$$r - \frac{n_H}{n_M} = \frac{2M}{mRT} \{ (P_A V_A - P_E (V_A + V_S)$$
$$+ (P_E V_S + P'_A V_A - P'_E (V_A + V_S) \} \quad (2)$$

Figure 4 shows the absorption isotherms in Pd measured in the ranges $2 \leqslant P$/bar $\leqslant 30$ and $433 \leqslant T$/K $\leqslant 573$ which agree well with the literature values [11].

The following procedure is followed in order to measure the desorption isotherms and hystersis in an alloy. After establishing the equilibrium pressure at any pressure P_E and the lowest temperature T_1, the temperature is raised slowly to the desired temperature T_2 at which the desorption point is to be measured. Some of the dissolved H in the alloy will be degassed and after some time, which depends on the sample, the desorption equilibrium pressure $P_{E'}$ at T_2 is noted and the corresponding hydrogen concentration is obtained from the knowledge of the original hydrogen concentration at T_1 and amount of hydrogen desorbed. This process is repeated for
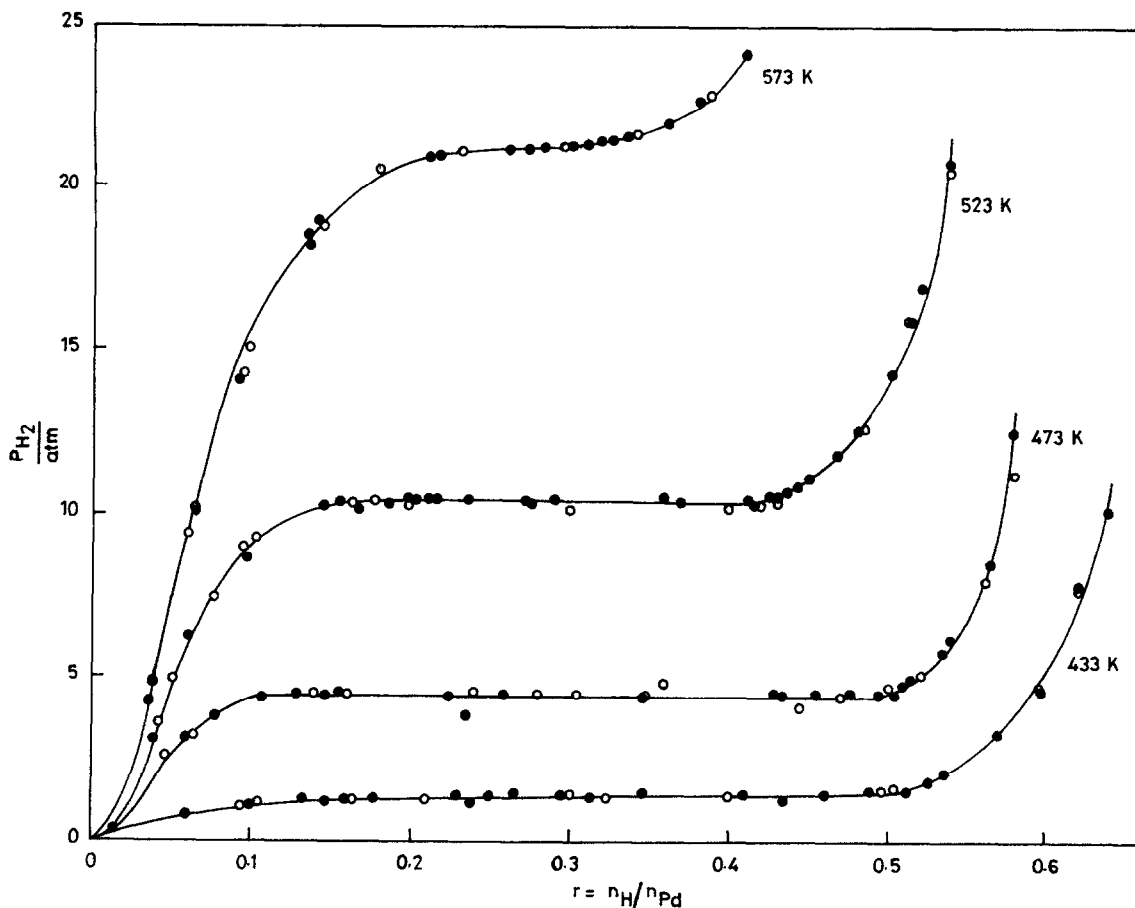
Fig. 4. Pressure–composition isotherms of palladium (● = present work; ○ = [11]).

different pressures and temperatures. From the absorption and desorption isotherms, the hysteresis and the plateau slope are obtained.

The kinetics of absorption of hydrogen by the alloy can be studied by recording the drop in the pressure versus time by connecting a chart recorder to the measuring system and the data is used for the evaluation of the kinetics of absorption by fitting into any one of the rate equations [12].

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