# Equipment for hydrogen absorption-desorption cycling characterization of hydride forming materials

G. Meyer, P. Arneodo Larochette, A. Baruj, and F. J. Castro
*Centro Atomico Bariloche, Instituto Balseiro, and CONICET, 8400 S. C. Bariloche, Argentina*

P. Lacharmoise and E. Zacur
*Centro Atomico Bariloche and Instituto Balseiro, 8400 S. C. Bariloche, Argentina*

B. A. Talagañis
*Centro Atomico Bariloche, Instituto Balseiro, and CONICET, 8400 S. C. Bariloche, Argentina*

Hydrogen storage materials suffer different degradation processes when they are cycled, forming and decomposing their associated hydride phases. In order to study these processes, we have designed and built an automated apparatus specifically developed for cycling samples of hydride forming materials by changing the external hydrogen pressure. Instead of the standard open configuration involving a high-pressure, high-quality gas bottle and a vacuum pump, the equipment uses another hydride forming material (in our case $LaNi_5$) as a source and sink of hydrogen. The resulting closed-loop configuration eliminates hydrogen waste and ensures that extremely high purity gas is used during the whole experiment, thanks to the purifying properties of the selected hydride as source/sink. Hydrogen pressure is set by changing the source/sink temperature. Cycles can be performed as fast as one cycle every 5 min, a period comparable with typical good hydride forming material kinetics. An example of application of the apparatus is given for 1000 absorption/desorption cycles on a $Mm_{0.8}Ca_{0.2}Ni_5$ sample. © *2007 American Institute of Physics.*
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## I. INTRODUCTION

Hydrogen storage materials are subjected to multiple hydriding/dehydriding cycles during their service life, which is, in turn, mainly determined by the material property degradation associated with such cycling processes.[1] For this reason, it is crucial to analyze the cycling behavior of these materials as early as possible during their designing or development stages. To do that, hydrogen absorption/desorption can be triggered either by changing the pressure or the temperature of small samples of the materials. Roughly, a cyclic process of degradation of them induced by pressure changes can be divided into two main components: A first one, called "intrinsic," is solely due to the interaction with hydrogen and is related to the progressive formation of more stable hydrides and/or phases that decrease the material's reversible behavior. A second one, "extrinsic," is related to the interaction with impurities which either occupy sites where hydrogen atoms could be adsorbed on the surface or form alternative crystallographic phases with the alloy components. In order to correctly analyze the material properties, i.e., the intrinsic process of degradation, it is necessary to minimize the presence of impurities in the gas stream. On the other hand, hydride formation/dissolution can also be achieved by lowering/increasing the temperature of the material. The degradation related to this type of cycling processes is usually due to the formation of stable phases at elevated temperatures presenting poor hydrogen storage properties.

Performing hydrogen pressure absorption/desorption cycles is time consuming and strict conditions must be met by the purity of the gas. Usually, experiments have been performed using standard Sieverts-type volumetric devices.[2,3] This kind of equipment is designed to precisely measure pressure-concentration-temperature (PCT) characteristics of materials, being not optimized for performing thousands of absorption/desorption cycles. For this reason, studies involving only a very limited number of cycles are frequently found in the literature.

Even in cases in which devices are designed specifically for pressure cycling, other problems arise. Typical designs of these devices involve the use of a high purity $H_2$ source and a vacuum pump used as a gas sink. The first problem related with this concept is immediately apparent: large quantities of high purity gas are wasted as cycling proceeds. For example, an equipment with an inner volume of 100 $cm^3$ working at 60 bar $H_2$ roughly needs 2/3 of a standard gas bottle ($8 \times 10^6$ SCCM) (SCCM denotes cubic centimeter per minute at STP) in order to perform 1000 cycles. A second and usually more important problem is related with gas purity itself. As mentioned before, hydride forming materials are poisoned by the presence of impurities such as $O_2$, $CO_2$, and water, among many others. Commercially available $H_2$ gas bottles are typically 99.99% grade, but 99.999% can also be obtained at a considerably higher price. This gas can be further purified, for example, up to 99.9999% grade by means of a hydriding/dehydriding process using a suitable material. Even in such a case, as the gas is pumped out of the system on every cycle, fresh gas must be constantly added to the

system through a gas inlet. This operation increases the risk of leakage and subsequent contamination. On the other side, the open sink concept (usually a mechanical vacuum pump) also introduces some risk of contamination due to, for example, oil fumes from the pump and gas upstream diffusion.

Some of these problems are avoided when the formation/ dissolution of hydrides is induced by thermal cycling. Purified $H_2$ is only introduced into the equipment's volume at the beginning of the experiment and, as long as all components are properly sealed, impurities are not expected to affect the degradation process. However, in order to completely dissolve hydrides, it is usually necessary to increase the temperature up to a point where stable phases can be formed by atomic diffusion. In this way, the resulting study of degradation is not only related to the hydrogen absorption/desorption processes but also to thermally induced changes. Moreover, it will probably be needed to cycle the sample apart from technological working conditions to facilitate hydriding/ decomposition, making the association of results with real applications difficult.

Considering all these problems, we have designed a fully automated equipment for pressure and/or temperature cycling based on a closed-loop concept. The basic idea is that a hydride forming material is used as a source/sink element by controlling its temperature. This design combines the advantages of thermal and pressure cycling devices. On one hand, when performing pressure cycling, what is thermally cycled is the hydrogen source/sink material and not the sample under study. High purity $H_2$ gas is introduced only once into the equipment at the beginning of the cycling process, and it is further purified by the source/sink hydride forming material. On the other hand, when performing thermal cycling, $H_2$ pressure at an intermediate volume can be adjusted by changing the temperature of the source/sink. This allows the sample to cycle material in a realistic manner, close to its expected working conditions. In the present article, we describe the design of this new machine, characterize its main working properties, and present a brief example of operation.

## II. THE EQUIPMENT

### A. Layout of the cycling device

Figure 1 shows a schematic diagram of the equipment. It can be divided into three main parts: (i) hydrogen source/ sink (HSS), (ii) intermediate volume, and (iii) sample reactor. The HSS (Fig. 2) consists of an inner cylindrical stainless steel recipient (23 mm diameter, 51 mm height, 1 mm wall thickness) containing a hydride forming material (from now on, the hydride) that acts as a sink of hydrogen when cooled down to room temperature (hydride forms absorbing the surrounding $H_2$ gas) or as a source when heated up to $100-200\ °C$ (hydride dissolves releasing $H_2$ gas). A resistive cartridge heater (Omega Chromalox CIR-1033 240 V-400 W) is enclosed in a tube placed in the axis of the hydride container. The heater, operated from the computer through a relay (R, in Fig. 1), can increase the temperature of the hydride up to $550\ °C$. The hydride container is surrounded by an external recipient that can be filled up with running tap water in order to attain a high cooling rate. A
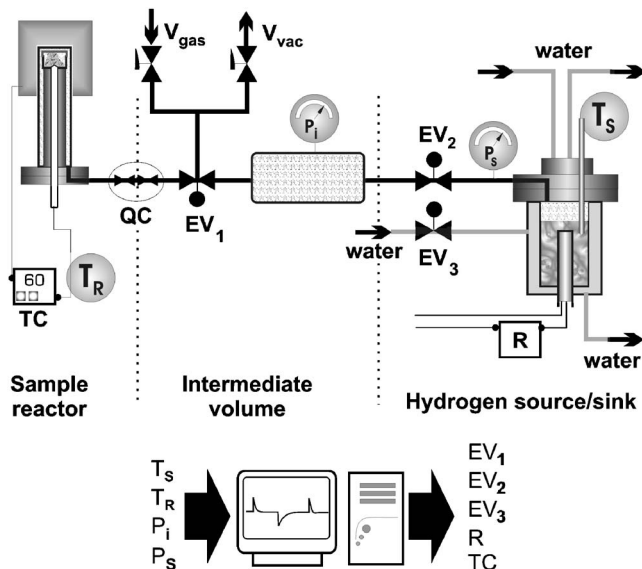


FIG. 1. Schematic layout of the cycling equipment. Three main parts can be distinguished: (i) the hydrogen source/sink (right), (ii) the intermediate volume (center), and (iii) the sample reactor (left). $EV_1$, $EV_2$, and $EV_3$; are electroactuated valves, controlled by the computer. R is the sink/source heater relay and TC the thermal controller for the sample, both components are PC controlled. $T_R$ and $T_S$ are the thermocouples for the sink/source and the sample, respectively. $P_s$ and $P_i$ are the pressure sensors for the sink/ source and the intermediate volume, respectively. QC is a quick-coupling connector. $V_{gas}$ and $V_{vac}$ are manual valves which allow connecting the system to $H_2$ injection and vacuum pump, respectively, at the beginning of operation.

standard watering electromechanical valve ($EV_3$, Rain Bird) operated via the personal computer (PC) switches on and off the water flow during the cooling and heating stages, respectively. This external recipient is emptied during heating stages by gravity. The inner hydride container has an upper stainless steel lid, which contains the $H_2$ inlet/outlet with a filter of 0.5 $\mu$m mesh in order to avoid losing material when charging/discharging the container. The lid hermetically seals
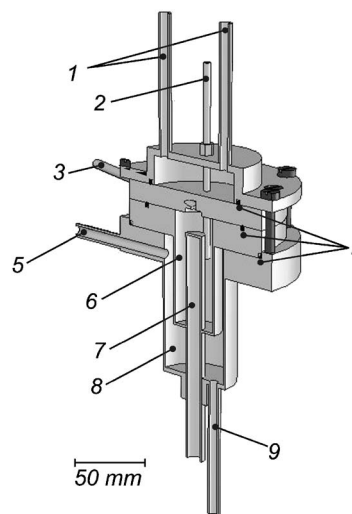


FIG. 2. Cut view of the hydrogen source/sink. (1) Water entrances for the upper cooling system, (2) $T_s$ thermocouple container, (3) $H_2$ inlet/outlet, (4) sealing o-rings, (5) water inlet for the lower cooling system, (6) hydride container, (7) heater compartment, (8) lower cooling water vessel, and (9) water outlet for the lower cooling system.
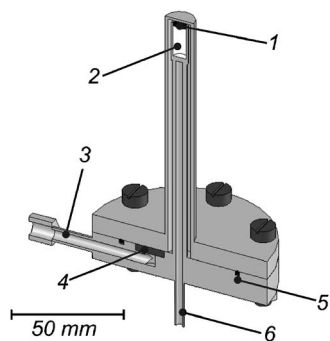
FIG. 3. Cut view of the sample reactor. (1) Sample container lid (2 $\mu$m mesh filter), (2) sample container, (3) H$_2$ inlet/outlet, (4) 0.5 $\mu$m mesh inlet/outlet filter, (5) sealing o-ring, and (6) $T_R$ thermocouple compartment.

the container with a silicon o-ring which can stand temperatures up to around 200 °C and is continuously refrigerated during operation. This action is accomplished by encasing the lid with an outer vessel through which water continuously flows during the experiments. Six $\frac{1}{4}$ in. steel bolts close the system by tightening the upper vessel part to the lower water recipient. O-rings are placed at contact surfaces to ensure the water tightness of the cooling system. The temperature of the hydride is measured by means of a $K$-type thermocouple ($T_S$) inserted in a tube which crosses the upper vessel upper lid and is inserted into the material's core. This tube is parallel to the hydride container axis but is located out of its center, halfway between the outside wall of the heater tube and the inner wall of the container. An ADZ Nagano SML-20.0-I pressure sensor ($P_S$) allows controlling the pressure of the container. The signals from this pressure meter and the thermocouple are processed by a PC and are also fed to independent comparator circuits which switch the heater's current off when the maximum pressure or temperature are exceeded, respectively. A Swagelok SS-42S4 valve (EV$_2$) integrated to a HOKE 0172L2 electromechanical valve actuator closes the container. The HSS (including valve EV$_2$) can be removed from the equipment while keeping its interior tightly closed. In this way, the container can be taken into a glove box in order to open and close it under an inert Ar atmosphere.

Valve EV$_2$ connects the HSS to an intermediate container. This stainless steel cylindrical container (110 cm$^3$) has a Bourdon Sedeme E914 pressure sensor ($P_i$) and is connected to a Swagelok SS-42XS4 three-way valve (EV$_1$). This valve was also automated using a HOKE 0172L2F electromechanical actuator and is used either to connect the volume to the sample reactor or with the external H$_2$ source and vacuum system. This second option is useful during the initial filling of the system and during the removal of hydrogen after operation. The internal volume of the container can be reduced, when necessary, by adding solid stainless steel cylinders of known volume.

The sample reactor (Fig. 3) is coupled to the system via a quick-coupling valve with internal shut-off, allowing an easy removal for manipulation inside a glove box. The sample reactor consists of an external stainless steel tube, containing an internal cylindrical sample holder. The sample is placed on top of the sample holder covered by a 2 $\mu$m

mesh filter lid. A thermocouple ($T_R$) is located in the lower part of the sample holder, in close contact with the floor of the sample container. The signal from this thermocouple is 100 times amplified and read by the PC. The holder is attached to the base of the reactor, which closes to the upper part with an o-ring seal and steel bolts. A gas inlet/outlet is placed in the lower part. A filter (0.5 $\mu$m mesh) is placed between the inlet and the inner volume. A resistive furnace can be externally attached to the upper end of the reactor in order to select the sample temperature during cycling. If necessary, a water cooler is placed below the furnace to avoid burning the sealing o-ring and to better define the temperature of the whole set. The furnace temperature is set by means of a proportional-integral-derivative (PID)-logic Eurotherm 2132 controller. This heating system could also be used to perform thermal cycling of the samples, although the equipment has not been designed specifically for this purpose.

## B. The hydride source/sink

As mentioned before, the advantages of using a hydride forming material as a source/sink of hydrogen are twofold: (i) the hydride acts as an on-line purifier of hydrogen, and (ii) the cycling process can be performed in a closed-loop configuration, avoiding hydrogen waste. Typical materials with these properties follow a Van't Hoff law of the type

$$\ln\left(\frac{p}{p_0}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}. \tag{1}$$

Here, $p$ and $p_0$ are the equilibrium pressures at temperature $T$ and at the reference point, $\Delta H$ and $\Delta S$ are the hydride formation enthalpy and entropy, and $R$ is the universal gas constant. Usually, for a given material, the relation between pressure and temperature both for absorption and desorption is plotted in a diagram using the reciprocal temperature as the ordinate axis and the logarithm of the pressure as the abscissa axis, resulting in characteristic parallel straight lines. The material is in the hydride phase when its condition lies above the lines and in the normal state when below. In this context, the conditions that the hydride should fulfill are presented in Fig. 4. High ($p_H$) and low ($p_L$) pressure conditions are achieved by increasing or lowering the temperature of the source/sink material between $T_H$ and $T_L$, respectively. If the reactor temperature ($T_R$) is properly chosen, the sample will undergo hydriding/dehydriding cycles as pressure conditions are changed by the source/sink material. In this case, we have chosen LaNi$_5$ as the source/sink material because it meets the following conditions: (i) hydride formation/dissolution at suitable pressures takes place in the range of temperatures between room temperature and 200 °C; (ii) these low/high pressures are in the range between 2 and 60 atm; (iii) the material has excellent sorption kinetics; and (iv) the material is quite resistant to pressure and temperature cycling. In addition, this is an alloy with well known properties,[4,5] allowing its easy and reliable integration into the designing process. Ideally, LaNi$_5$ can store up to 1.49 wt % of hydrogen.[4] Then, taking into account the volume of each different container in the equipment, it is necessary to fill the reactor with at least 40 g of LaNi$_5$ for at-
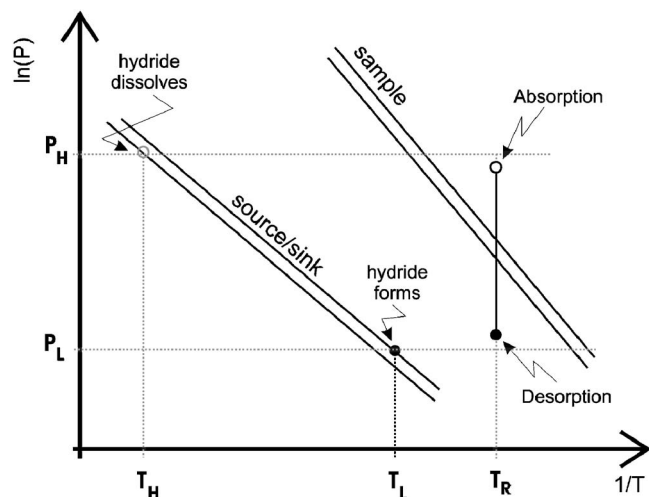
FIG. 4. Schematic van't Hoff diagram illustrating the working principle of the equipment. When the temperature of the source/sink material is raised up to $T_H$, the hydride dissolves in order to reach an equilibrium pressure $P_H$. When the sample at temperature $T_R$ is brought in contact with that high pressure, its hydride phase forms. On the other hand, lowering the hydride source/sink temperature down to $T_L$ results in a low equilibrium pressure $P_L$, which the material attains by absorbing the surrounding $H_2$ gas. This pressure $P_L$ is well below the equilibrium pressure for the sample's hydride, so hydrogen is desorbed from it.

taining a $H_2$ pressure of 60 bars. One disadvantage of $LaNi_5$ is its poor thermal conductivity.[5,6] In order to overcome this problem, we have mixed $LaNi_5$ and Cu powders. Cu powder was previously subjected to a reduction treatment (12 h at 350 °C under flowing $H_2$). It can be shown that 87:13 $LaNi_5$:Cu mix increases the thermal conductivity by a factor of 40.[6]

During operation, $LaNi_5$ is also subjected to cycling conditions. These conditions result in a progressive degradation of its properties, an effect reported in the literature.[7] Typically, this degradation makes it difficult to obtain the limit pressures after around 3000 cycles. However, there is also a well established procedure for recovering the full properties of $LaNi_5$. It consists in baking the material at around 400 °C under dynamical vacuum conditions.[7] The design of the HSS allows performing such treatment *in situ* while keeping the sample under controlled conditions. Then, in principle, there is no limitation in the number of cycles one can perform using this machine, as long as $LaNi_5$ is periodically reconstituted.

### C. Control electronics and software

The experiment control and data recording is performed via a PC using a MicroAxial RIAC QFD16-DA data acquisition card (DAC) and a monitor/control software designed in our laboratory. The DAC has eight 16 bit analog inputs, four bidirectional input/outputs, and an 8 bit digital output. Analog inputs receive signals from the pressure meters $P_s$ and $P_i$ (see Fig. 1) and the amplified signals from thermocouples $T_s$ and $T_r$. An analog output is used to set the parameters for the reactor temperature controller, and four digital signals are devoted to energize the relays which actuate the electromechanical valves $EV_1$, $EV_2$, and $EV_3$, and switch on and off the source/sink heater ("R" in Fig. 1). These relays

(Microaxial MTB-Opto) are optocoupled in order to isolate the PC from the electric power line. The software was written using MS VISUAL BASIC 6.0. It can register different users, each of whom can save and retrieve different sets of experiment parameters in order to facilitate the general use of the equipment. The initial window provides access to the different modules of the program.

(i)     Setup of the equipment parameters: depending on the user permissions, it can manipulate different properties, for example, vessel volumes, calibration curves of pressure and temperature detectors, and maximum source temperature.

(ii)    Setup of experiment parameters: this feature allows setting low- and high-pressure limits, reactor temperature, total number of cycles, time limits, and sample characteristics.

(iii)   Measurement: the program acts on the different components of the equipment (valves and heaters) in order to accomplish the desired sequence of operation. A constantly updated pressure versus time plot at the intermediate volume is displayed in this window. The program includes two different kinds of cycles. During the so-called "normal" cycles, only the total amount of hydrogen absorbed or desorbed by the sample are recorded in a text file. In addition, during "detailed" cycles, the amount of hydrogen in the sample against time is continuously recorded and saved in separated files. The duration and frequency of these detailed cycles can be chosen before starting the cycling sequence. This distinction between normal and detailed cycles results in an economy of information which, otherwise, would be very difficult to treat afterwards due to its usually large volume.

(iv)    Manual operation: this window provides full access to the different components of the equipment, allowing an easy operation of each of them out of a cycling sequence, mainly used for getting sample properties and calibration purposes.

Due to security considerations, the program does not allow certain operations, for example, turning the source heater on while the $EV_2$ valve is closed or while the water valve $EV_3$ is opened.

## III. OPERATION OF THE EQUIPMENT

### A. Overview

Usually, a cycling experiment starts by loading a known amount of a given sample into the reactor. This operation takes place inside a glove box under controlled Ar atmosphere. Once the reactor is coupled to the equipment via a quick-coupling connector QC (Fig. 1), the system is thoroughly evacuated by opening valve $V_{vac}$ and $EV_2$, and setting valve $EV_1$ alternatively connecting the reactor with the intermediate volume and the intermediate volume with the vacuum pump. After this step, valve $V_{vac}$ is closed and $H_2$ gas is injected into the system by setting valve $EV_1$ connecting the intermediate volume with the gas bottle while opening valves $V_{gas}$ and $EV_2$ (Fig. 1). During this stage, water
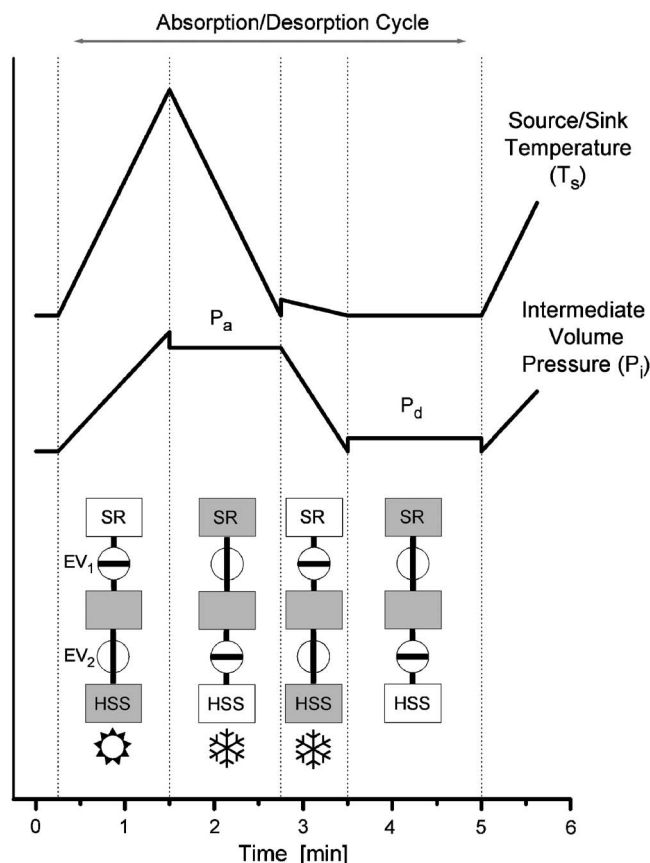
FIG. 5. Scheme of an absorption/desorption cycle showing the evolution of pressure at the intermediate volume, the source/sink temperature, and the state of different components of the system. HSS denotes the hydride sink/source element, SR is the sample reactor, and $EV_1$ and $EV_2$ are the electro-actuated valves, as described in Fig. 1.
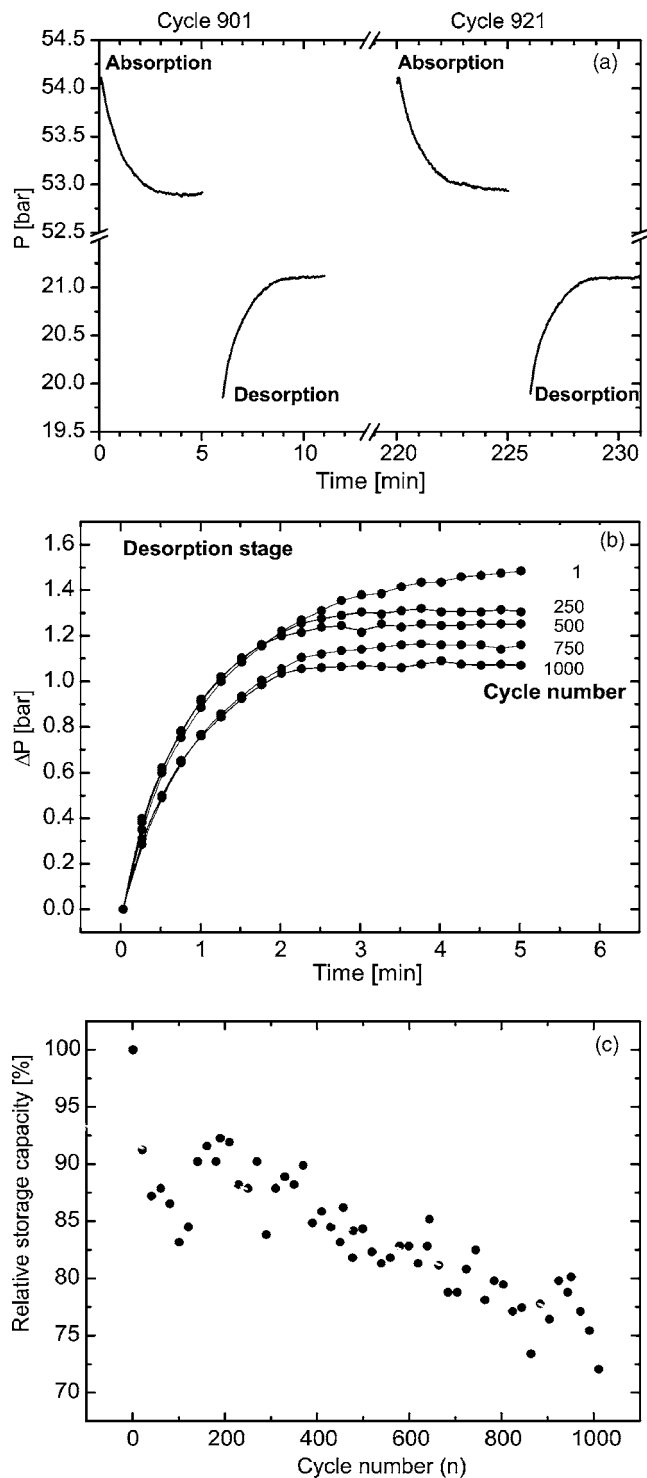


FIG. 6. Results obtained in a real cycling experiment performed on a $Mm_{0.8}Ca_{0.2}Ni_5$ sample at 25 °C. (a) Example of two particular detailed cycles (901 and 921 in the cycling sequence). The upper curves correspond to the absorption of hydrogen by the sample, and the two lower ones to the desorption process. (b) Comparison between the desorption stages corresponding to different cycles. (c) Evolution of the hydrogen storage capacity of the sample as the cycling process proceeds.

valve $EV_3$ is opened in order to keep the material cold because hydride formation is an exothermic process. This operation is performed until the hydride inside HSS is almost completely formed; then valve $V_{gas}$ is closed.

At this point, the system is ready for performing cycles. Each cycle consists of an absorption stage and a desorption stage. Figure 5 shows the time dependence of operational properties during one cycle. The absorption stage starts by closing valve $EV_3$, opening $EV_2$, and powering on the HSS heater. Hydrogen is released by the hydride and the pressure at the intermediate volume ($P_i$) increases. Temperature ($T_s$) and pressure ($P_s$) at the HSS are constantly monitored by the program and compared with preset limit values. Once $P_i$ reaches the absorption pressure set beforehand, the HSS heater is switched off, valve $EV_3$ opened, and valve $EV_2$ closed. The reactor is then put in contact with the intermediate volume when valve $EV_1$ is opened and the sample starts the absorption process at pressure $P_a$. This process finishes either when time or pressure limits are reached. The absorption stage ends at this point beginning the subsequent desorption stage. Valve $EV_1$ closes the reactor and valve $EV_2$ opens to connect the intermediate volume with the already cooled HSS. Hydrogen is reabsorbed into the hydride until the desired lower $P_i$ level is reached. Then, $EV_2$ is closed and $EV_1$ connects the reactor with the intermediate volume. Hydrogen release by the sample is followed by recording the pressure,

a process that, again, stops by time or pressure limits. An important detail is that the program takes into account the final pressure on each vessel when calculating the starting pressure for different operations. For example, if the reactor was left at high pressure after an absorption stage, before

TABLE I. Limit values for different operational parameters.

| Source/Sink | $m_{source}$ | 50 g ($LaNi_5$+Cu powder) |
|---|---|---|
| | $T_{min}/T_{max}$ (operation) | 15 °C/150 °C |
| | $T_{max}$ (annealing) | 400 °C |
| Sample | $m_{sample}$ | ~1 g |
| | $P_{min}/P_{max}$ ($H_2$) | 2 bars/60 bars |
| | $T_{min}/T_{max}$ | 22 °C/400 °C |
| | $t$ (4 bars→60 bars) | 2 min |
| | $t$ (60 bars→4 bars) | 3 min |

starting the desorption stage, the intermediate volume pressure would reach a level below the set lower limit in order to achieve that set value when reconnecting this volume to the reactor. The cycling process continues in the described way until the desired number of cycles is obtained. Finally, the system is evacuated and left ready for further use. The equipment can perform a full cycle in about 5 min. However, the real duration of the cycles will usually be determined by the sample sorption kinetics. The results consist of several files, depending on the number of detailed cycles performed. One file contains the starting and ending pressures for the absorption and desorption stages for each cycle. This file allows following the evolution of the total amount of hydrogen absorbed/released by the sample as a function of the number of cycles. In addition, files containing the information gathered during periodic detailed cycles provide a way to follow the changes in the sorption kinetics as cycling proceeds.

The cycling experiments can be carried out within the limit values presented in Table I.

## B. Example

As an example of application of the apparatus presented here, we have cycled a material which belongs to the $AB_5$ family of storage alloys as the $LaNi_5$ used in the HSS. However, in the studied alloy, expensive La is replaced partially by Mm (mischmetal, a mixture of rare earth elements) and by Ca with the goal of obtaining an affordable alternative for technological applications. The sample, 1 g of commercial $Mm_{0.8}Ca_{0.2}Ni_5$, was cycled 1000 times between 19.8 and 54.1 bars at a constant temperature of 25 °C. An interval of 2.5 min was set for performing absorption and desorption stages, which resulted in a cycle period of about 7 min. Every 20 so-called normal cycles, a detailed cycle was per-

formed. During detailed cycles, the time allowed for absorption and desorption was doubled to 5 min. The complete cycling experiment took about five working days. Figure 6(a) shows an example of two of the detailed cycles, namely, cycles 901 and 921 in the experiment sequence. The upper curves show the absorption stages, while the lower ones correspond to desorption processes. There, it can be seen that sorption starts soon after opening $EV_1$ valve and that after around 2 min a plateau is reached. Figure 6(b) shows the evolution of desorption kinetics as a function of the number of cycles. The first cycle is quite different to the subsequent ones. This difference is probably related with a process of activation, where new material surface is created as the original powder particles break due to the volume difference between the matrix and the forming hydride, and planar defects accumulate in the material. After the first cycle, the plateau is reached after 2 min independently on the cycle number. However, a reduction in the storage capacity is observed and plotted in Fig. 6(c). As it can be seen there, the cycling process is responsible for a progressive reduction in the storage capacity of the material. The final reduction of about 20% can be attributed to a disproportion process, usual in this kind of material, although further analysis involving diffraction methods and magnetic measurements is necessary to fully understand the phenomenon.[8] These results provide an example of the experiments which can be performed using this equipment.

## ACKNOWLEDGMENTS

[1] D. Chandra, J. J. Reilly, and R. Chellappa, JOM **58**, 26 (2006).
[2] J. S. Han, M. Pezat, and J. Y. Lee, J. Less-Common Met. **130**, 395 (1987).
[3] J. M. Park and J. Y. Lee, Mater. Res. Bull. **22**, 455 (1987).
[4] G. Sandrock, J. Alloys Compd. **293–295**, 877 (1999).
[5] P. D. Goodell, G. D. Sandrock, and E. L. Huston, J. Less-Common Met. **73**, 135 (1980).
[6] S. Suda, Y. Komazaki, and N. Kobayashi, J. Less-Common Met. **89**, 317 (1982).
[7] P. D. Goodell, J. Less-Common Met. **99**, 1 (1984).
[8] K. Suzuki, K. Ishikawa, and K. Aoki, Mater. Trans., JIM **41**, 581 (2000).