Thermochimica Acta, 24 (1978) 369–381

A HIGH-TEMPERATURE, HIGH-PRESSURE MICROBALANCE FOR THE DETERMINATION OF THE HYDROGEN SORPTION CHARACTERISTICS OF METAL HYDRIDES*

H. M. LUTZ, R. SCHMITT AND F. STEFFENS
Battelle-Geneva Research Centre, CH-1227 Carouge (Switzerland)

ABSTRACT

The use of hydrogen as a future complementary energy vector is essentially linked to the problem of its storage and transport. Apart from conventional techniques, the storage of hydrogen in metal hydrides is considered of interest for a number of applications. To make a metal hydride a suitable hydrogen storage material, it must exhibit certain characteristics concerning in particular: (i) the hydrogen storage capacity, (ii) the dissociation pressure–temperature relationship, (iii) the heat of reaction, and (iv) the kinetics of hydrogen absorption/desorption. All these data can be determined using a microbalance capable of operating at high temperatures and pressures.

The principal item of the thermogravimetric installation developed at Battelle-Geneva consists of a Sartorius balance type 4406 equipped with a heatable autoclave. The attached pressure and temperature control systems allow measurements under conditions of constant pressure (10^{-5} Torr to 60 bar) and temperature (15 to 600°C), as well as the execution of pressure and temperature cycling programs at various scanning speeds.

The performance and versatility of the instrument is illustrated by measuring various hydrogen sorption characteristics of the known magnesium nickel hydride and iron titanium hydride.

INTRODUCTION

In view of the potential of hydrogen as a non-polluting fuel and future complementary energy vector, the problem of its storage and bulk transport has recently found much consideration. Apart from the conventional techniques, such as compression and liquefaction, the chemical storage of hydrogen in the form of metal

---

* Presented at the 14th Conference on Vacuum Microbalance Techniques, Salford, 27th–28th September 1976.

hydrides[1, 2] could offer a solution to this problem, in particular for applications requiring relatively high storage densities and safety.

In order to enable the evaluation of a metal hydride for a specific hydrogen storage application, knowledge of several of its physico-chemical properties is essential. This concerns in particular:

(i) the massic hydrogen storage capacity

(ii) the equilibrium pressure–temperature relationship

(iii) the heat of hydride formation/dissociation

(iv) the kinetics of hydrogen absorption/desorption

(v) the effect of repeated absorption/desorption cycling on the hydride performance.

For determining these data, several experimental methods could be envisaged. However, no instrument would be of similar versatility as a microbalance which, furthermore, allows easy automation and registration of nearly all of these measurements. An additional advantage of the gravimetric method in comparison to volumetric techniques often used in metal hydride research has to be seen in the fact that any diffusion of hydrogen through the apparatus walls will remain of no consequence on the results obtained.

Since most metals do not react with hydrogen under normal conditions of pressure and temperature, an apparatus was designed to permit measurements in the temperature range of about 15 to 600°C and in the pressure range of 10^{-5} Torr to 60 bar. These values were chosen in conformity with the ranges of interest for a practical hydride application.

BASIC CONSIDERATIONS OF METAL HYDRIDES

The storage of hydrogen as metal hydride is based on the reversible reaction of a metal or alloy (Me) with gaseous hydrogen following the equation:

$$x\mathrm{Me} + y\mathrm{H}_2 \underset{\text{dissociation}}{\overset{\text{formation}}{\rightleftarrows}} \mathrm{Me}_x\mathrm{H}_{2y} \mp |\Delta H|$$

All hydrides suitable for hydrogen storage purposes are formed by exothermic reaction: the more negative the value of the heat of formation (ΔH), the more stable is the hydride. Consequently, the dissociation of a hydride is an endothermic process and requires the addition of heat.

The hydrogen weight contents of a hydride as a function of temperature and pressure can be obtained from composition-pressure-isotherms (CPI) for the corresponding metal–hydrogen system. At a given temperature, the hydride phase is in equilibrium with a certain hydrogen pressure. For the two-phase region metal hydride, indicated by a plateau in the CPI-diagram, the dependence of the equilibrium pressure on the temperature is described by the Van 't Hoff equation:

$$\log P_{H_2} = -\frac{A}{T} + B$$

The equation determines the thermal stability of a hydride, i.e., its readiness to dissociate if either the temperature is increased or the pressure decreased. From the constants A and B in this equation, the thermodynamic functions can be calculated according to:

$$A = \frac{\Delta H_T^0}{4.57}; \qquad B = \frac{\Delta S_T^0}{4.57}$$

Since, under equilibrium conditions, the apparent rate of hydrogen exchange is zero, a measurable absorption/desorption of hydrogen can occur only when the metal/hydride is subjected to certain minimum pressure and temperature conditions off equilibrium. Apart from the difference between operating and equilibrium conditions, the chemical nature of the metal and the surface properties will influence the kinetics of the hydride formation and dissociation.

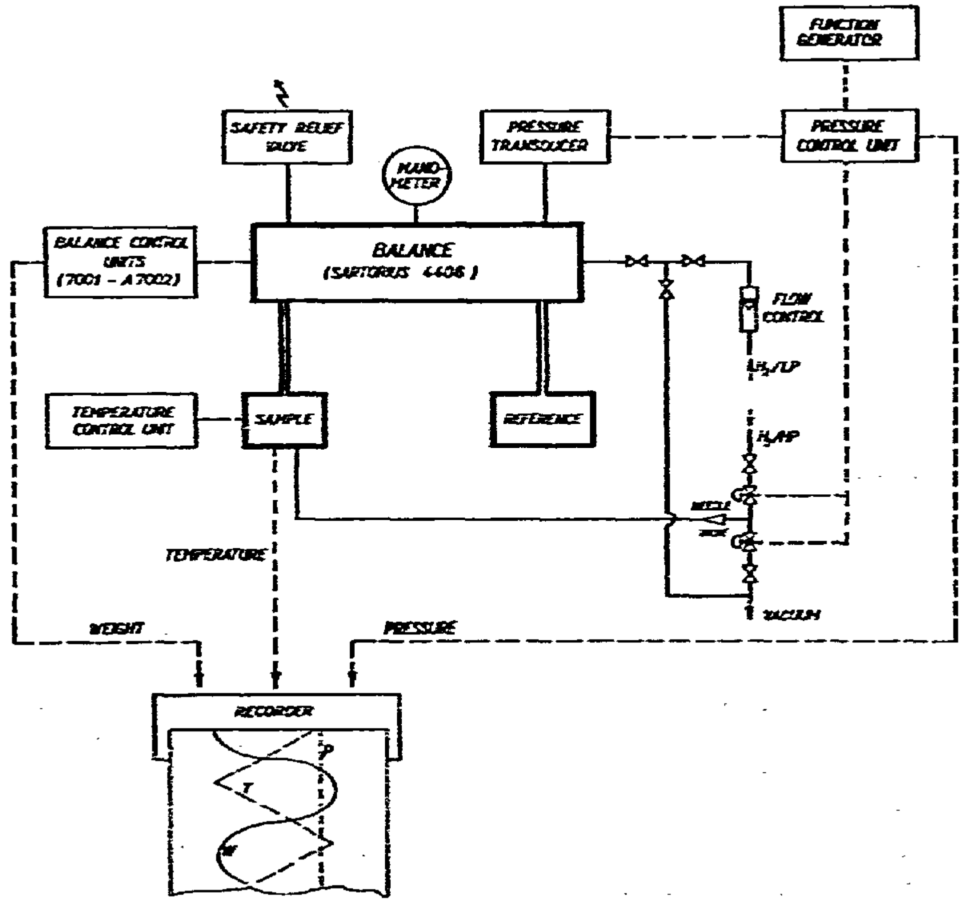


Fig. 1. Schematic diagram of the thermogravimetric installation.

DESCRIPTION OF THE APPARATUS

A schematic diagram of the thermogravimetric installation is shown in Fig. 1. The principal item of this set-up is a Sartorius electronic high-pressure microbalance (Type 4406) designed for a maximum operating pressure of 150 bar. The maximum weighing capcity is 25 g and the sensitivity 1 μg.

The hangdown tube on the sample side of the balance is equipped with a heatable autoclave designed and built at Battelle-Geneva. The autoclave is turned out of one piece of stainless-steel SS 316. Its cover consists of a Varian high-vacuum flange which is attached by six screws to the autoclave. Sealing is provided by means of a gold-plated copper gasket. The flange is welded to the lower end of the tube which in the weld zone is equipped with a water-cooling jacket.

Six heating elements are fitted into the autoclave wall; an embedded NiCr–Ni thermocouple is used for the temperature regulation. A gas inlet tube with a thermocouple lead through is welded into the base of the autoclave. The interior thermocouple, being placed just underneath the quartz pan, measures the sample temperature. A few windings of stainless-steel tubing for water circulation around the exterior autoclave diameter enable fast cooling rates even at lower temperatures. Water cooling can be switched on and off automatically by means of an electromagnetic valve at any preset temperature below 250°C.

The temperature control unit incorporates a standard proportional controller with fast cycling and a triac-switching element. The programmer consists of a step-motor driven 10-turn Helipot. The motor speed is adjusted by frequency control of the stepping rate. The heating or cooling rate can be varied between 10 and 240°C h^{-1}. The 10-turn dial attached to the potentiometer gives a direct reading of the temperature. Upper and lower limits of the temperature cycle are set by two 10-turn potentiometers, and whenever one of these limits is reached the direction of the programming potentiometer is reversed. In this way, a triangular wave of very low frequency can be created. If required, other temperature profiles may be obtained by the use of an external generator. Apart from the step motor, the whole circuit is solid state.

The pressure-control system of the apparatus incorporates mainly a pressure transducer, the control unit, and two electromagnetic valves. An electronic pressure transducer of the integrated circuit type (LX 1440 A of National Semiconductors Corp.) with a pressure range of zero to 68 atm and an overall precision of 0.5% is used. This transducer offers a high output voltage, 10 V for 68 atm, and has a vacuum reference incorporated.

The pressure-control unit consists of the various power supplies and a very stable reference voltage. A 10-turn potentiometer allows the setting of a voltage corresponding to the desired pressure. An electronic circuit of extremely high sensitivity permits pressure control within ± 0.1%.

Apart from constant-pressure operation, the pressure in the balance system can also be programmed by means of an external function generator. It is for instance possible to impose linear pressure cycling between preset limits at various scanning speeds or to perform stepwise pressure changes.

Two electromagnetic valves with on/off control, installed in the vacuum and high-pressure hydrogen line, regulate the systems pressure. In order to prevent pressure under- or overshoot, a manually operated needle valve limits the gas flow to and from the apparatus. The vacuum line is connected to a rotary pump, the high-pressure line to a gas cylinder containing hydrogen of required purity.

A safety circuit automatically shuts-off the high-pressure valve, whenever the deviation of the system pressure from the set value exceeds 0.5 bar which may be due e.g. to leakage. A by-pass to this safety device enables rapid pressure increase in the balance as is needed, for example, for measurement of the hydrogen absorption kinetics. Furthermore, a mechanical safety relief valve is installed to prevent any accidents and damages of the equipment.

A permanently installed precision Bourdon manometer is used for the calibration of the electronic pressure transducer and for independent pressure readings.

Moreover, the thermogravimetric installation provides the possibility of high-vacuum operation ($\sim 10^{-5}$ Torr) by means of a separate vacuum connection. A low-pressure supply system permits measurements in flowing hydrogen under atmospheric pressure.

A three-channel analog recorder measures sample weight, temperature and pressure simultaneously as a function of time. The use of an X–Y recorder allows direct tracing of the weight change as a function of pressure or temperature, which is particularly interesting for the determination of composition-pressure-isotherms.

Effects of pressure and temperature on the balance indications: Since the present installation incorporates only one heatable autoclave on the sample side, corrections of the direct reading of the balance indications are necessary. They are made by means of a reference manipulation with an inert sample under the same conditions of pressure, temperature and weight. At higher pressures and temperatures, convection effects are observed resulting in an oscillating of the weight and temperature curves. In order to eliminate or reduce convection effects and weight corrections, a symmetrical system where tare and sample are always kept at the same temperature will be used in future.

APPLICATION OF THE INSTRUMENT

The applicability and versatility of this equipment will be illustrated by some measurements of the hydrogen sorption properties of the known magnesium nickel hydride[3] and iron titanium hydride[4, 5].

Experimental

The preparation and activation (i.e., the first hydriding) of the Mg_2Ni and FeTi base alloys were made with reference to the techniques described by Reilly and Wiswall[3, 4]. Starting from high purity metals, the alloys were obtained by induction melting under argon and, thereafter, characterized by X-ray analysis. The alloys were then transferred to a glovebox with argon atmosphere and pulverized to a particle size of 0.5 to 1 mm for Mg_2Ni, and less than 33 μm for FeTi.

Three-hundred to 500 mg alloy samples, accurately weighed to ± 0.1 mg, were then introduced into the balance for activation and measurements. For activation, the FeTi and Mg_2Ni samples were subjected to an alternate treatment in high vacuum at 350 and 450°C, respectively, and in hydrogen under a pressure of 50 bar at 25 and 250°C, respectively. The activation process and its advancement were controlled by means of weight, temperature and pressure recordings, and was generally complete within five to ten cycles.

For both the activation and all the measurements reported in this paper, high purity hydrogen (99.997% H_2) was used.

Hydrogen storage capacity

To determine the quantity of hydrogen exchanged during the absorption or desorption process, the high-pressure microbalance can generally be used in two ways:

(i) By pressure variation at constant temperature, CPI-diagrams are obtained; they can be traced directly by x–y recording of the weight change as a function of the hydrogen pressure.

(ii) By temperature variation at constant pressure, absorption/desorption isobars are obtained; the curves can be traced either directly by x–y recording for single cycles, or indirectly from the weight and temperature variation as a function of time as measured with the 3-channel recorder. The latter method is especially useful for investigating the long-term absorption/desorption cycling behaviour of hydrides.

(a) *Determination of CPI-diagrams.* The hydrogen pressure in the balance system can be decreased or increased either continuously or stepwise. In the case of continuous pressure variation, the shape of the isotherms depends on the pressure scanning speed and reflects the kinetics of hydrogen exchange. This is shown in Fig. 2 for the dissociation of Mg_2NiH_4. With increasing rate of pressure decrease, the slope of the plateau in the desorption isotherm becomes steeper and the hydrogen desorption faster. This has to be expected, since equilibrium conditions are left more rapidly

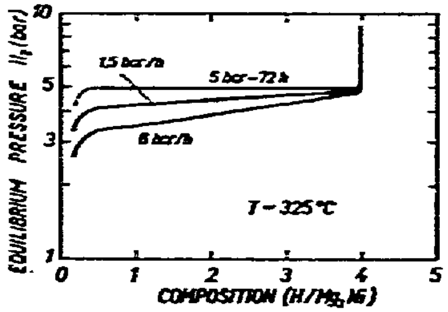
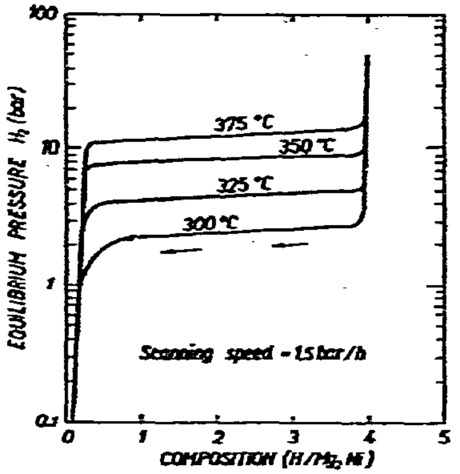


Fig. 2. Influence of the pressure scanning speed on the shape of the desorption isotherm at 325°C in the Mg_2Ni–H_2 system.



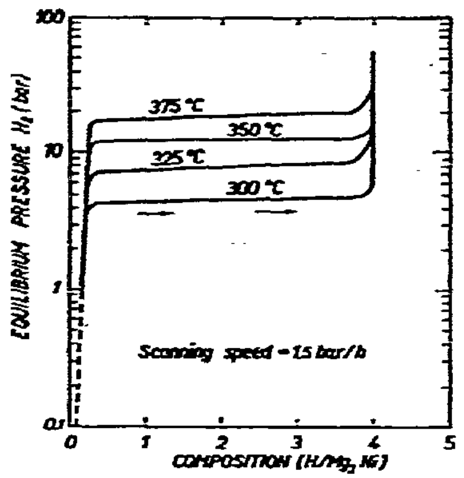
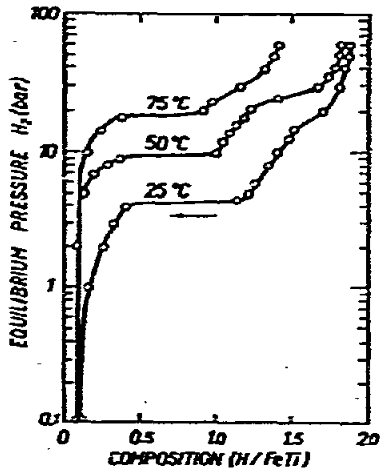


Fig. 3. Desorption isotherms for the Mg_2Ni-H_2 system at various temperatures.

Fig. 4. Absorption isotherms for the Mg_2Ni-H_2 system at various temperatures.



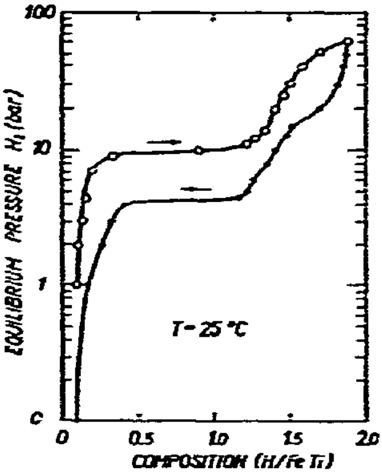


Fig. 5. Desorption isotherms for the $FeTi-H_2$ system at various temperatures.

Fig. 6. Hysteresis in the $FeTi-H_2$ system at 25 °C.

too. The equilibrium dissociation pressure, given by the bend in the isotherm, is much less affected by the scanning speed.

Therefrom, it becomes apparent that the appropriate pressure scanning speed must be chosen in accordance with the kinetics of hydrogen absorption/desorption and the desired accuracy of the results to be obtained. For quick screening tests or a first location of the plateau pressure region, high scanning speeds are preferred, since measurements will require much less time (factor 100 in Fig. 2). For exact determination of the CPI-diagram, the interesting pressure zone can then be rescreened at a much slower rate, or by stepwise pressure changes.

The desorption and absorption isotherms for the Mg_2Ni-H_2 system at various temperatures measured by the dynamic method are presented in Figs. 3 and 4, respectively. From these diagrams, the plateau reaction is found to be

$$Mg_2NiH_{0.2} + 1.9\ H_2 = Mg_2NiH_4 \qquad (1)$$

corresponding to a reversible hydrogen content of 3.4 wt.-%. The form of the isotherms indicate that the solubility of hydrogen in both the metal and hydride phase is very low. Furthermore, a hysteresis is observed in this system, the absorption isotherms being located at a higher pressure than the desorption isotherms for a given temperature. But for the maximum hydrogen concentration of the hydride, being reported as $Mg_2NiH_{4.3}$, the results obtained are in good agreement with those of Reilly and Wiswall[3].

For the determination of the CPI-diagram for the FeTi–H_2 system, the method of stepwise pressure increase/decrease was chosen, owing to the low rate of hydrogen exchange. Some desorption isotherms are presented in Fig. 5, a complete absorption/desorption cycle showing a hysteresis effect in Fig. 6. For some of the measuring points in the plateau region, more than 100 h were required to approach equilibrium.

The isotherms exhibit two plateaus, the higher one not being very pronounced. The length of the lower plateau seems to diminish as the temperature increases. Owing to pressure limitations of the instrument, the second plateau could not be completely obtained at higher temperatures. According to the isotherms at 25°C, the two reactions and the corresponding reversibly-exchanged amounts of hydrogen are:

$$FeTiH_{0.1} + 0.53\ H_2 = FeTiH_{1.16};\ 1.0\ \text{wt.-\%}\ H_2 \qquad (2)$$

$$FeTiH_{1.16} + 0.36\ H_2 = FeTiH_{1.88};\ 0.68\ \text{wt.-\%}\ H_2 \qquad (3)$$

(b) *Determination of absorption/desorption isobars.* Similar to the effects of pressure scanning, the slope of the absorption/desorption isobars is influenced by the rate of temperature decrease/increase. Shown in Fig. 7 are the absorption and desorption isobars for the Mg_2Ni–H_2 system obtained at different temperature

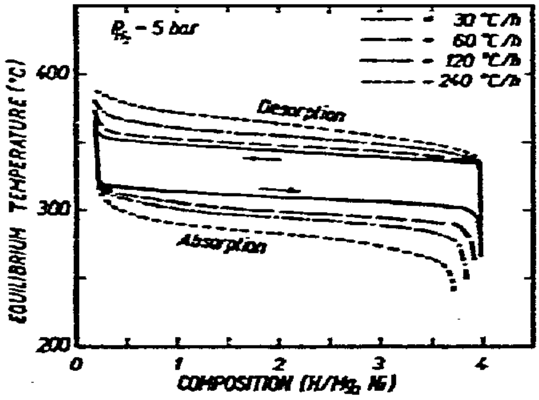
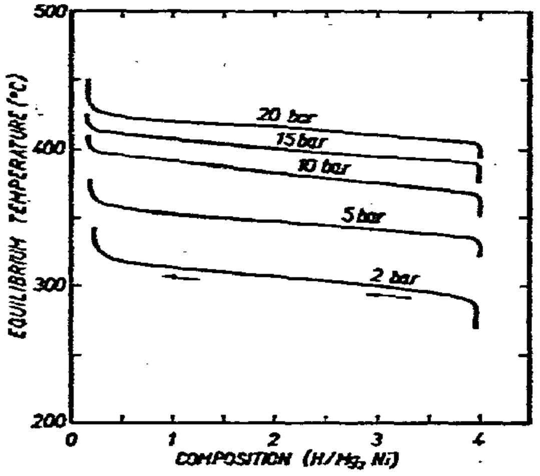


Fig. 7. Influence of the temperature scanning speed on the shape of the absorption and desorption isobars at 5 bar in the Mg_2Ni–H_2 system.



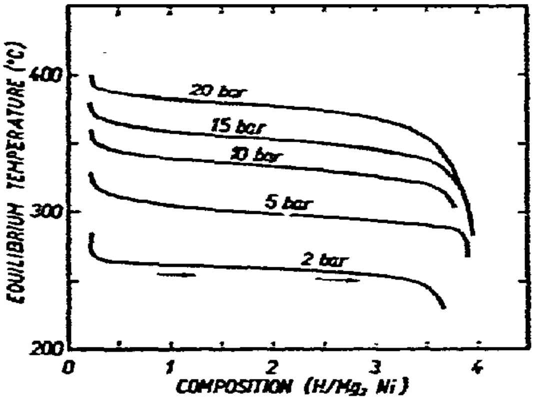
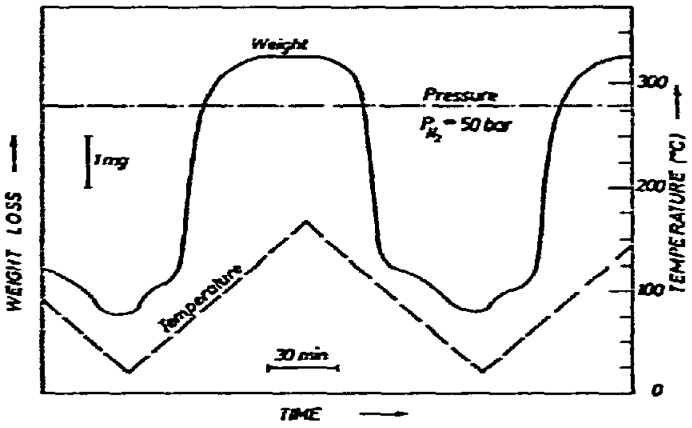


Fig. 8. Desorption isobars for the Mg_2Ni–H_2 system at various pressures.

Fig. 9. Absorption isobars for the Mg_2Ni–H_2 system at various pressures.



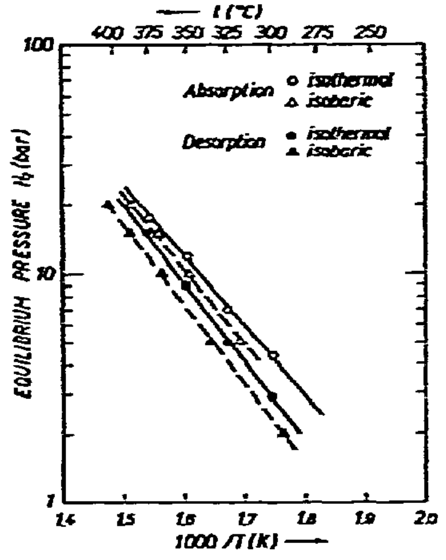


Fig. 10. Thermal cycling of $FeTiH_x$ at a rate of 2°C min^{-1} under a hydrogen pressure of 50 bar (weight of hydrogen-free sample: 320 mg).

Fig. 11. Equilibrium pressure–temperature relationship for the Mg_2Ni–H_2 system.

scanning speeds. As can be seen, the difference between absorption and desorption temperature, i.e., the hysteresis, becomes smaller when the temperature cycling rate diminishes ($\Delta T = 80$ and 35 °C at 240 and 30 °C h^{-1}, respectively). Below a certain value, 30 °C h^{-1} in this particular case, no further reduction of the hysteresis occurs. This can be explained by the fact that for a measurable hydrogen exchange to take place, a minimum temperature deviation from the equilibrium temperature is necessary. It further indicates that the hysteresis is a kinetical phenomenon.

Several desorption and absorption isobars for the Mg_2Ni–H_2 system obtained by automatic temperature cycling at a rate of 60°C h^{-1} are shown in Figs. 8 and 9, respectively. The form of the absorption isobars, in particular that at 2 bar, indicates a slow rate of hydriding at lower temperatures.

(c) *Determination of the cycling behaviour.* Figure 10 shows a section of the diagram obtained during thermal absorption/desorption cycling of $FeTiH_x$. The weight curve exhibits the two plateaus in accordance with the CPI-diagram. Owing to kinetic limitations at the chosen cycling conditions, the second plateau reaction is only incomplete and, consequently, the totally exchanged hydrogen amounts only to 1.54 wt-%. This type of diagram allows easy determination of the reversible hydrogen contents as a function of the number of absorption/desorption cycles performed. This is of importance for investigating the thermal stability of a hydride and the possible influence of the hydrogen purity on its cycling lifetime. Moreover, the temperatures of hydride formation and dissociation at a given pressure can be deduced from the diagram.

Pressure–temperature relationship and thermodynamic data

The pressure–temperature relationship for the plateau region can be obtained from both isothermal and isobaric measurements. A semilog plot of the equilibrium pressures vs. the reciprocal of the absolute temperature gives a straight line which obeys the equation $\log P_{\text{bar}} = (-A/T) + B$.

For the Mg_2Ni–H_2 system, the data of Figs. 3, 4, 8 and 9 were used to establish the four lines in Fig. 11. Therefrom, the values of the constants A and B are derived as summarized below:

	A	B
Isothermal absorption	3096	6.037
Isobaric absorption	3448	6.379
Isothermal desorption	3425	6.446
Isobaric desorption	3333	6.367

From the mean values for $A = 3325$ and $B = 6.307$, the thermodynamic values for reaction (1) are calculated to be $\Delta H_f^\circ = -15.2 \pm 1$ kcal/mol H_2; $\Delta S_f^\circ = -25.8 \pm 2$ cal/K mol H_2; and $\Delta G_f^\circ = -6.6 \pm 1$ kcal/mol H_2.

In Fig. 12 the pressure–temperature relationship for the first plateau reaction in the FeTi–H_2 system is given, based on the measurements reported in Fig. 5. The constants A and B of the equation are 1370 and 5.23, respectively. Thus, the thermodynamic data of dissociation for reaction (2) are $\Delta H_d^\circ = 6.3 \pm 1$ kcal/mol H_2; $\Delta S_d^\circ = 23.9 \pm 2$ cal/K mol H_2; $\Delta G_d^\circ = -0.8 \pm 1$ kcal/mol H_2. The thermodynamic values obtained for the two hydrides are in good correspondence with those reported by Reilly and Wiswall[3, 4] and Pick and Wenzl[5].

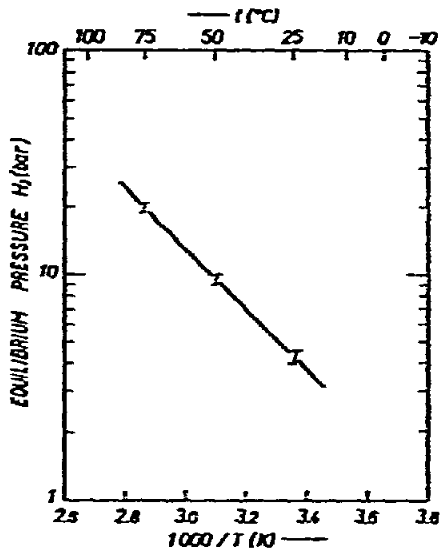
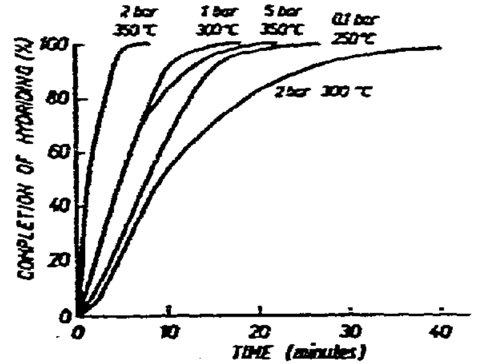


Fig. 12. Equilibrium dissociation pressure–temperature relationship for the FeTi–H_2 system.

Reaction kinetics

Determination of the rate of hydrogen exchange is performed on a semi-automatic basis. This means that the measuring conditions in the balance system have to be manually adjusted while the absorption/desorption process, once initiated, proceeds under automatic control.

Theoretically, hydriding and dehydriding can be induced by both temperature and pressure variation as shown before. However, owing to the heat capacity of the autoclave, only the pressure variation will lead to satisfactory results. At a given temperature, the sample is subjected to a hydrogen pressure under which the metal or hydride phase is stable. By rapid pressure increase or decrease to the required value, by manual operation, an unstable state is created and, consequently, hydrogen exchange starts. The maximum achievable rate of pressure change is in the order of



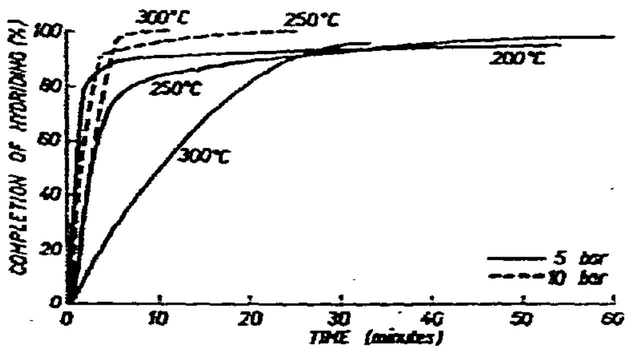


Fig. 13. Kinetics of dehydriding Mg_2NiH_4 at various pressures and temperatures.

Fig. 14. Kinetics of hydriding Mg_2Ni to Mg_2NiH_4.

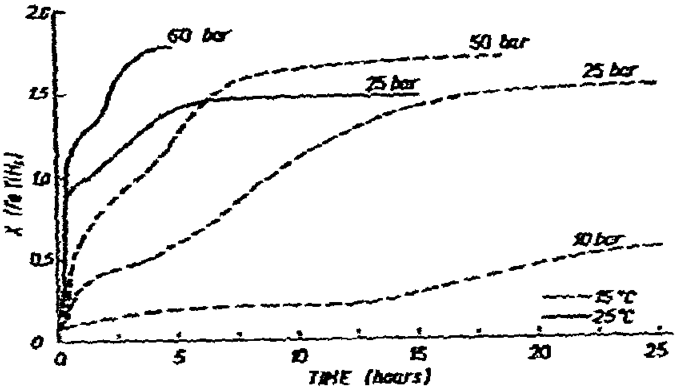


Fig. 15. Kinetics of dehydriding FeTiH$_x$ (<33 μm) at different pressures at 25 and 50°C.

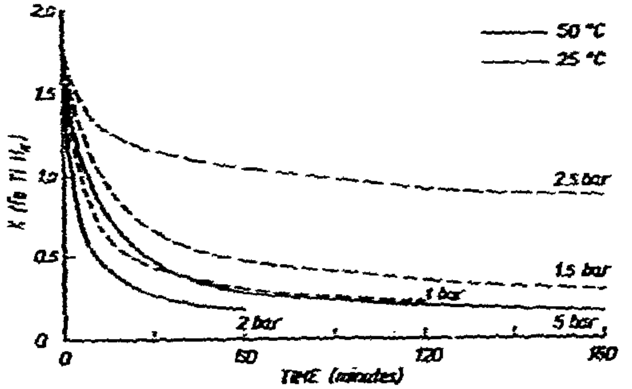


Fig. 16. Kinetics of hydriding FeTi (<33 μm) at different pressures at 15 and 25°C.

20 bar per minute. However, in view of the reaction rates normally observed with metal hydrides, this source of error is negligible. Rapid hydrogen absorption/desorption is accompanied by a transient temperature increase/decrease of the sample owing to the reaction heat. Since the sample mass generally is only around 500 mg, this effect should be of secondary importance too.

By recording the weight variation as a function of time, diagrams as presented in Figs. 13 and 14 for Mg_2NiH_4 and in Figs. 15 and 16 for $FeTiH_x$ are obtained. The possibility of varying the paper transport speed of the 3-channel recorder applied between 2 cm h^{-1} and 60 cm min^{-1} guarantees a good resolution and enables direct tracing of the absorption and desorption curves over a wide range of reaction rates.

CONCLUSIONS

A thermogravimetric installation for measurements at high temperatures and pressures and for the execution of pressure and temperature cycling programs especially adapted to the peculiarities of metal hydrides has been built. The instrument performance has been demonstrated by means of isothermal, isobaric and kinetical absorption/desorption measurements for the Mg_2Ni-and FeTi-hydrogen system.

The most important physico-chemical properties of Mg_2NiH_4 and $FeTiH_{\sim 2}$ have been determined. With its range of capabilities, this installation has to be considered a unique instrument for metal hydride research in particular and for the investigation of gas–solid reactions in general.

REFERENCES

1 J. J. Reilly, R. H. Wiswall, K. C. Hoffman and C. H. Waide, *7th Alternative Automotive Power Systems Division Contractors Coordination Meeting, Ann Arbor, Michigan, May 1974.*
2 K. D. Beccu, H. Lutz and O. de Pous, *Chem.-Ing. Techn.*, 48 (1976) 161.
3 J. J. Reilly and R. H. Wiswall, Jr., *Inorg. Chem.*, 7 (1968) 2254.
4 J. J. Reilly and R. H. Wiswall, Jr., *Inorg. Chem.*, 13 (1974) 218.
5 M. A. Pick and H. Wenzl, *Proc. of the 1st World Hydrogen Energy Conf.*, 8B-27, Univ. of Miami, Coral Gables, Fla., 1976.