DEVELOPMENT OF A NEW THERMOGRAVIMETRIC AND CALORIMETRIC TECHNIQUE FOR THE DETERMINATION OF ENERGETICS, THERMODYNAMICS AND KINETICS OF HYDROGEN STORAGE IN VARIOUS MATERIALS

P. LE PARLOUËR[1], C. MATHONAT[2]
[1]Thermal Consulting, 35 Chemin de Crépieux, BP142, 69643 Caluire Cedex, France
leparlouer@thermalconsulting.com
[2] SETARAM Instrumentation, 7 rue de l'Oratoire, 69300 Caluire. France
mathonat@setaram.com

Keywords: hydrogen storage, thermogravimetry, calorimetry, absorption, desorption

Abstract

The recent developments in the field of fuel cells and more particularly hydrogen storage under solid form have underlined the usefulness of the thermogravimetry (TG) under pressure of hydrogen to define the PCT (Pressure Concentration Temperature) curves. Such a PCT curve will define the capacity of storing hydrogen for a given metal or organic compound as a function of the temperature and the pressure.

The calorimetric techniques (DSC) enable also to perform such studies at variable temperature and pressure, in order to determine the energy associated with the adsorption or desorption of hydrogen. The knowledge of this energy allows to assess the increase in temperature in the course of the reaction. This parameter will be very helpful for the industrialization and the safety of the storage process.

Setaram develops an original combination of both thermogravimetric and calorimetric measurements that has the great advantage of being able to correlate both pieces of information (mass variation and energy) on the same sample under hydrogen pressure.

The new thermogravimetric and calorimetric technique will apply for any material used for hydrogen storage under solid form (metal hydride, borohydride, alanate, zeolite, clathrate …).

1. Introduction

Most of the technologies that are developed for the characterization of materials, and especially nanomaterials, are dedicated to structural analysis and surface characterization (Auger spectroscopy, X- Ray diffraction, Neutron diffraction, Atomic Force Microscopy,…), but very few researches have been performed on the thermal characterization of the nanopowders, nanofibers or nanotubes.

In order to fill this gap, Setaram is developping an innovative technique for this field of expertise that will combine the thermogravimetric and calorimetric techniques to operate under high pressure of various types of gas. The thermogravimetric technique, by measuring the mass variation of the sample, provides information on gas diffusion from or into the material. The calorimetric technique measures the corresponding heat exchange due to the thermal phenomenon. Both techniques give a direct access to the kinetics of the transformation or reaction occurring within the material according to the temperature and the gas pressure.

The experimentations on nanomaterials require very high sensitivity that are not mostly available from the existing equipments. This is especially true when it is needed to measure the capacities of absorption and desorption of the new nanomaterials to be used in specific applications. Nanomaterials are very interesting in this field as they exhibit a larger specific area. Most of these types of experiments have to be run under pressure, and in some applications with reactive gas.

2. Thermogravimetric and calorimetric techniques for hydrogen absorption and desorption

For the investigation of conventional H-storage materials, **thermogravimetry (TGA)** under pressure of hydrogen is of the most common and highly accurate technique to define the PCT (Pressure Concentration Temperature) curves. Such a PCT curve will define the capacity of storing hydrogen for a given metal and metal-organic compounds as a function of the temperature and the pressure. A second technique, based on a **volumetric** system, is commonly used in the field of metal hydrides. This technique is very sensitive, but doesn't enable to performed kinetics measurements at strictly constant pressure. On the other hand, the commercial TGA instruments that are available on the market require a significant amount of materials. This requirement is hardly fulfilled for nanomaterials such as nanocrystals, nanopowders, nanocomposites. With a limited amount of sample, the limit of detection of the balance becomes the critical point to be solved. The innovative technical solution enables to reach a very high sensitivity that is required to accurately measure the hydrogen absorption and dissociation of the nanomaterial.

Up to now, most of the laboratories interested in this field only use the thermogravimetric technique uniquely. However, it is known that an exothermic effect is linked to the hydrogen absorption process depending on the materials. The knowledge of this energy allows assessing the increase in temperature during the course of the reaction. This parameter is very important to be known for the industrialization and the safety of the storage process. In case of an exothermal absorption, a too large increase of temperature will stop the refueling process by reaching the equilibrium conditions. On the other hand, in case of exothermic absorption, with the high surface area nanomaterials, as the chemical reactivity is increased, this thermal effect has to be particularly checked on the safety point of view. Moreover, it is strongly difficult to performed isothermal kinetics measurements.

The best instrumental solution is to combine a calorimetric measurement during the thermogravimetric test on the same sample. The **calorimetric technique (DSC)** enables to perform studies at variable temperature and pressure, in order to determine the energy associated with the absorption or desorption of hydrogen.
The innovative combination of both thermogravimetric and calorimetric measurements under pressure has the unique advantage to correlate both pieces of information (mass variation and energy) on the same sample.
The equipment will provide the unique and precise information needed for fundamental and practical analyses that cannot be obtained neither by only using the present thermogravimetric PCT systems, but nor by using volumetric PCT systems that are wrongly operating in the case of marked exo- and endothermal reactions

In the case of nanomaterials, it is very important to work on the same sample in order to afford problems of sampling especially critical with the size and the surface of the nanoparticles. From such a new TG-DSC combination, the results are made out of significance to describe properly the thermodynamics and kinetics of the reactions.

The new thermogravimetric and calorimetric technique will apply for any metal hydride material used for hydrogen storage under solid form (crystalline powder, thin film, nanolayer, nanocomposite…).

A very important task in the development of the instrument is to meet the requirements of ATEX directive for the use in potentially explosive atmospheres (especially hydrogen).
The main applications of the new high pressure TG-DSC technique in the field of hydrogen storage are:

- the hydrogenation characteristics of various H-storage materials, especially nanomaterials
- the reversibility of the reaction
- the improvement of their production and synthesis
- the optimization of the temperatures of adsorption and desorption
- the influence of the addition of catalysts
- the safety conditions for the process (especially the absorption phase)
- the kinetic evaluation of the reaction
- the extrapolation and application to industrial hydrogen storage

3. The new SENSYS High Pressure DSC
Setaram (France) has been developing and manufacturing high pressure DSC and calorimeters for more than 30 years with a technology that is perfectly adapted for the operation under pressure (Figure 1). Today the maximum pressure that can be reached with the DSC instruments is equivalent to 1000 bar.

Figure 1 : The SENSYS DSC

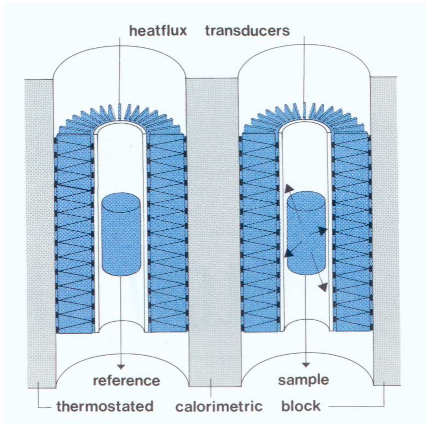

Figure 2 : The CALVET calorimetric principle

Setaram is the only company producing a DSC based on the Calvet principle (Figure 2). Instead of using a plate (or 2D) detector, the DSC detector has a 3D fluxmeter that completely surrounds the sample (contained in a crucible). This technology provides many interesting advantages:

- the total heat is transfered through the 3D detector, providing a very high accuracy to the calorimetric measurement
- the sensitivity of the DSC detector is independent of the nature and the pressure of the gas
- an absolute calibration of the DSC detector is performed using an electrical method (Joule effect)
- the DSC cell is built around an open tube that allows pressurization on a limited volume.

But the main advantage of using such a technology is that only the sample is under pressure in the container, and not the whole DSC detector as most of the other High Pressure DSC

instruments. The volume under pressure is very limited, that increases the safety conditions for such a test.
Setaram has developed specific high pressure containers as described on the figure 3

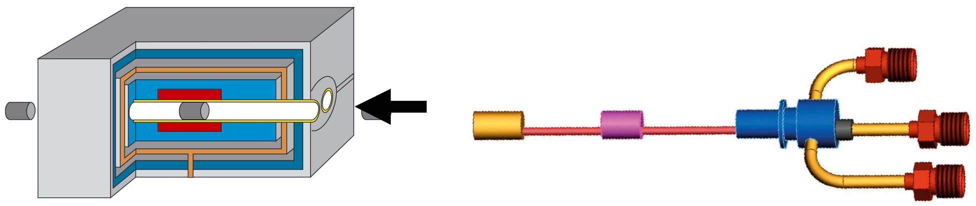

Figure 3: The High Pressure vessel for the SENSYS DSC

The HP vessel is made in incoloy and can work with a current pressure of 400 bar. A dedicated high pressure panel is used to fix the pressure in the vessel containing the material. The vessel is closed using a screwable stopper and reusable.

4. The new SENSYS High Pressure TG-DSC
Most of the so-called TG-DSC instruments that are on the market, are derived from the TG-DTA principle. In all the situations, the DSC detector is attached to the balance and located in a furnace. The SENSYS TG-DSC (Figure 4) uses a completely different technological approach. The DSC and the TGA are two distinct detectors that are combined for TG-DSC measurements, but are also used as regular DSC and TGA equipments (Figure 5). The main advantage of this combination is that the specifications, especially the sensitivity, of the DSC and TGA detectors are not compromised by the simultaneous measurement. Moreover, the TGA measurement is run symmetrically, as sample and reference are located in different tubes on each side of the beam of the balance. The symmetrical set-up allows perturbations generated by heating to be cancelled (buoyancy effect) and to generate measurements with very small mass variations to be obtained (less than 1 µg). Such a TG-DSC combination guarantees very accurate DSC and TGA data on the same sample.

Figure 4 : The SENSYS TG-DSC

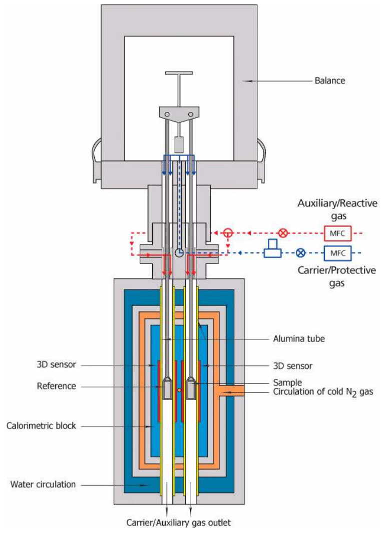

Figure 5: Principle of the SENSYS TG-DSC

Up to now such a TG-DSC instrument is working under normal pressure.

However the Calvet DSC technology (described in the previous paragraph) is adapted to work under pressure in a closed vessel, but also in an open tube in a flow mode. Such a high pressure device is used for the investigation of the hydrogen uptake of metallic alloys up to 100 bar (1,2,3).
A similar Setaram balance has also been adapted to work under hydrogen high pressure for investigation of magnesium hydrides (4).
The innovative technology will combine strong expertises to produce an unique TG-DSC instrument working under high pressure, with all the technological requirements needed for the ATEX certification. The new instrument will be able to work under high pressure (maximum pressure: 100 bar) in a range of temperature from -120°C to 400°C.

Even if the new instrument is designed to work under high gas pressure, it will also apply to work under reduced pressure (excellent primary vacuum). This option is especially interesting first to outgas any materials before operating the adsorption process, secondly but better important for the control of adsorption processes. Anyway, many hydrides are thermodynamically too stable for hydrogen storage purposes at room temperature. However in terms of hydrogenation, some organic or metal-organic reactions require disposal of rather stable hydrides, or encapsulated particles as hydrogen bonding vectors. The low pressure coupled TG-DSC apparatus will be a unique instrument for R & D purposes.
A second very important option is the possibility to connect a gas analyzer online with the TG-DSC instrument. This combination enables to analyze the gas emitted by the material during the transformation or the reaction, providing qualitative information on the chemical process. Once more, a perfect control of parallel monitored measurements is needed since chemistry combines mass combination and heat formation.

5. Applications of the new thermal analysis techniques

The new thermal techniques are developed to work for hydrogen storage science, dedicated to materials and more specifically to any metal hydride under solid form (crystalline powder, thin film, nanolayer, nanocomposite, even comprising so-called catalysts as few additives…).
The new measurement techniques are used to analyze the thermodynamics and kinetics of the materials reaction, to obtain the following data:

- the hydrogenation characteristics of vary various H-storage materials
- the reversibility of the reaction, thus up to long term cycles
- the improvement of their production and synthesis, comprising the multidefect state at processing
- the precise determination of the temperatures of adsorption and desorption, for further optimisation
- the influence of the addition of nanocatalysts, especially to understand the concomitant steps process
- the safety conditions for the process (especially during absorption phase)
- the kinetic and thermodynamic evaluation of the reaction

Some examples of applications are given below.

- **Hydrogen storage in magnesium hydride MgH_2 (DSC scanning mode)**

The needs to have a specifically a DSC analyzer working under gas pressure can be immediately understood since the enthalpy of formation of metal hydride can reach high values (up to 1/4 to 1/3 of that involved in hydrogen combustion to form H_2O).

A major challenge is to well understand the chemical parameters of the formation of reversible metal hydrides. The SENSYS High Pressure DSC is used to investigate this reversibility (absorption and desorption) under 20 bar of hydrogen in a heating and cooling modes.
The determination of the different enthalpies (absorption: -1067 J/g and desorption: 1104 J/g) correlate the good reversibility of the investigated material. The thermogram also gives the corresponding temperatures of absorption and desorption.

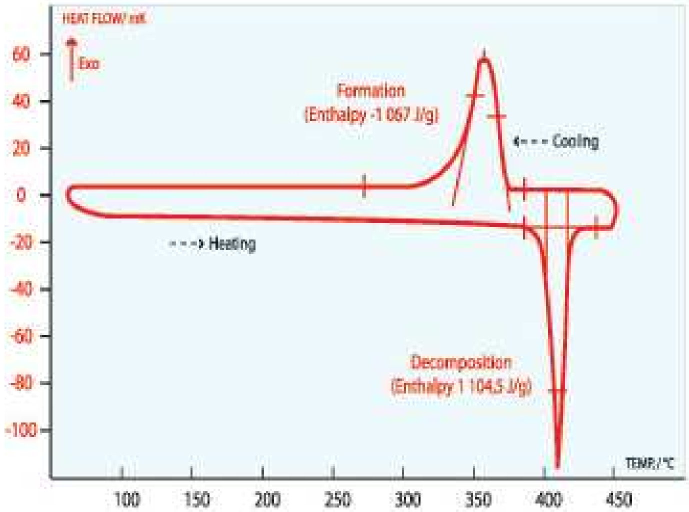

Figure 6: Absorption and desorption of hydrogen in magnesium hydride in scanning mode

- **Hydrogen storage in a magnesium alloy (DSC isothermal mode)**

Such a hydrogen storage investigation can also be run at a constant temperature using the SENSYS High Pressure DSC. The magnesium alloy contained in the High Pressure vessel under 1 bar hydrogen is heated up to 400°C (temperature of absorption noticed on figure 6). Then the pressure is increased up to 40 bar H_2. The corresponding exothermic effect of absorption is measured. After maintaining the material during one hour in an isotherm/isobar mode, the pressure is decreased down to 1 bar giving the endothermic peak of desorption. A good correlation of the absorption (-1094 J/g) and desorption (1081 J/g) enthalpies is noticed

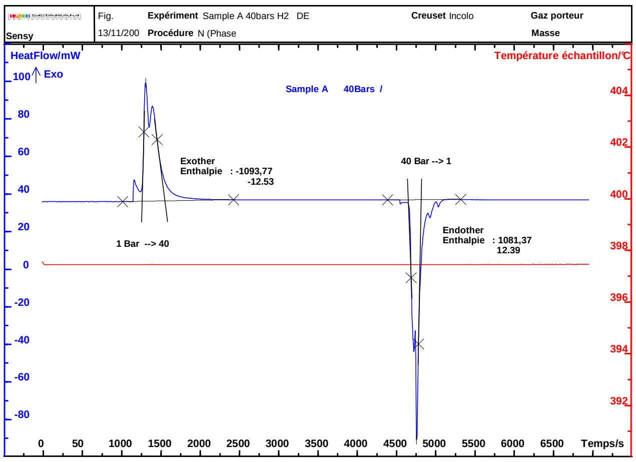

Figure 7: Absorption and desorption of hydrogen in magnesium alloy in isothermal mode

- **Thermal decomposition of ammonia borane**

Ammonia borane (BH_3NH_3) or borazane, is a stable solid with high hydrogen content (about 20 mass%). A thermally activated decomposition of borazane takes place in the temperature range 350–410 K accompanied by hydrogen release and heat evolution (Figure 8) (5). The SENSYS TG-DSC is the ideal technique to investigate these two types of phenomena (heat and mass loss) on the same material.

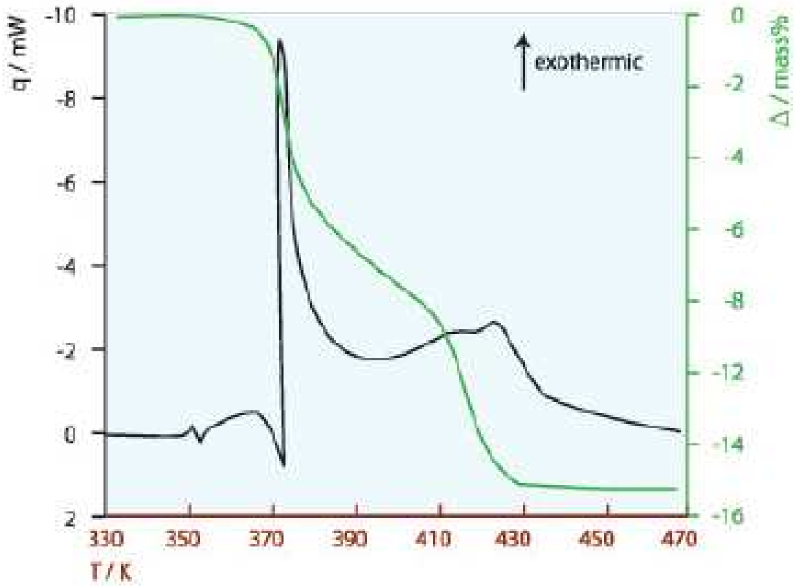

Figure 8: TG-DSC investigation of the decomposition of ammonia borane

The endothermic melting of borazane at 370K is followed by two successive exothermic decomposition of the sample, producing hydrogen. The measurement of the mass loss allows to determine the hydrogen content in the material. The integration of the exothermic effects will provide the corresponding heat of dissociation for the same sample.

6. Conclusion

Such new instruments give the unique opportunity to make accessible thermodynamics and thermal principles of gas solid reactions for a large range of materials and especially all types of materials used for hydrogen storage. The novel developed instruments can be applied for any material reactivity to gas in powder form as soon as there is an interest to characterize its synthesis or transformation under various atmospheres, versus both Temperature and Pressure (T&P), to evaluate the thermal behaviour versus T&P, to measure absorption and desorption capacities in any types of gases versus T&P, to evaluate its thermal stability at cycle versus T&P.

References

1- J. K. Lomness, M. D. Hampton and L. A. Giannuzzi, International Journal of Hydrogen Energy 27 (2002) 915-920

2- M.D. Hampton and J.K. Lomness, International Journal of Hydrogen Energy 24 (1999) 175-187

3- M. Resan, M.D. Hampton, J.K. Lomness and D.K. Slattery, International Journal of Hydrogen Energy 30 (2005) 1413-1416

4- M. Bououdina, J. L. Soubeyroux, P. Juen, C. Mouget, R. Argoud and D. Fruchart, Journal of Alloys and Compounds 231 (1195) 422-426

5- F. Baitalow, J. Baumann, G. Wolf, K. Jaenicke-Robler, G. Leitner, Thermochimica Acta 391 (2002) 159-168