

Simultaneous TDS–DSC measurements in magnesium hydride

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Received 1 June 2002; accepted 26 October 2002

Abstract

Decomposition of MgH_2 has been studied by means of simultaneous thermal desorption spectroscopy (TDS) and differential scanning calorimetry (DSC). Measurements have been accomplished in an experimental set-up composed of a differential scanning calorimeter connected through a capillary tube to a mass spectrometer. The experimental system allows the simultaneous determination of the heat absorbed by and the hydrogen evolved from MgH_2 during its thermal decomposition. The H-desorption from magnesium hydride samples non-exposed to air has been studied. The desorption curves are analysed with a nucleation and growth formalism and kinetic parameters are obtained.

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Keywords: Thermal analysis; Thermal desorption spectroscopy; Hydrogen desorption kinetics; Hydrogen storage materials

1. Introduction

Thermal desorption spectroscopy (TDS) is a technique used to determine the desorption kinetics of volatile species from solids. It was first developed in relation to surface science studies but lately has also been applied to the study of other solid state problems and, in particular, to the study of the decomposition of metal hydrides [1–5]. In this context, the kinetics of hydrogen desorption from a metal can be investigated and the slowest step of the hydride decomposition analysed. In addition, the technique can be used to investigate the energy distribution of hydrogen sites in the metal lattice. All this information is quite relevant to improve the characteristic time of hydride formation/decomposition, a key parameter for applications, e.g. metal hydride batteries or metal hydride storage units.

In most cases, the information obtained from TDS experiments in metal hydrides is difficult to interpret because hydrogen desorption takes place simultaneously with several other processes, e.g. surface modifications, amorphous-crystalline phase transitions or solid state reactions [6–8]. On the other hand, all these processes can be studied by means of calorimetric techniques such as

reaction calorimetry or differential scanning calorimetry (DSC) [9–12], where the heat evolved or absorbed by the sample during the transformation is recorded as a function of sample temperature or elapsed time.

The simultaneous use of different techniques to obtain information of any physical-chemical process is always very helpful for the analysis and understanding of such processes. Recently, the coupling of thermal-analysis and gas analysis techniques (DSC–MS, TG–MS, TG–IR, etc.) has become very popular [13] due to the potential to simultaneously measure the absorption heat and mass desorbed from the sample during its decomposition.

In this paper, we present a kinetic study of the decomposition of magnesium hydride. The measurements have been accomplished in a new experimental system composed of a differential scanning calorimeter (DSC) connected through a capillary tube to a quadrupole mass spectrometer (MS) for TDS measurements [14].

2. The experimental system

The experimental apparatus used for the coupled TDS–DSC measurements has been described previously [14]. For the sake of clarity, a brief review of the main characteristics is given.

The system is sketched in Fig. 1. It is composed of a commercial DSC-4 Perkin-Elmer differential scanning

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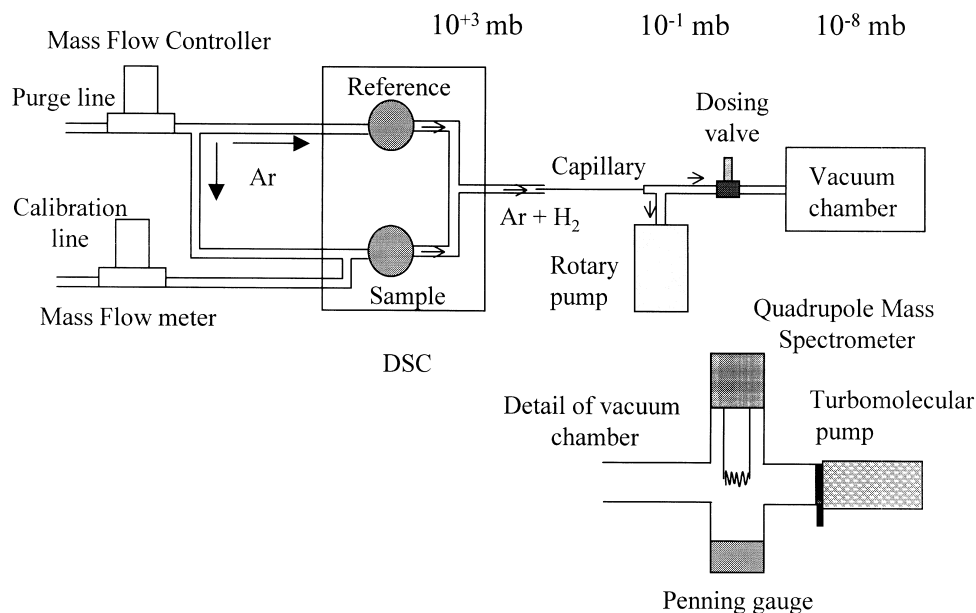


Fig. 1. Experimental set-up used for the simultaneous DSC–MS measurements.

calorimeter and a vacuum chamber equipped with a quadrupole mass spectrometer (QMS 200 Balzers) for gas analysis. Both systems are connected through a thin capillary tube (0.23-mm inner diameter) which can be heated up to 200 °C to avoid vapor condensation. The metal hydride sample (typically ≤ 10 mg, but it can be as low as 0.01 mg) is held in an aluminium pan located in a double-furnace system for DSC measurements. An empty aluminium pan is used as a reference. A controlled flux of a carrier gas (Ar) is passed through the DSC system while a linear heating ramp is imposed on both aluminium pans. The carrier gas, Ar, and the gas evolved from the sample, H_2 , are extracted from the DSC system by a vacuum gradient imposed in the capillary tube. About 1% of the Ar– H_2 mixture is conducted through a dosing valve to the high vacuum chamber, which is equipped with the quadrupole mass spectrometer. The instantaneous H_2 -ion current measured by the MS appears to be proportional to the hydrogen desorption rate from the sample, and the whole equipment set-up forms a TDS system.

The experimentally measured area under the MS curve can be related, by means of a proper calibration of the system, to the number of H-moles released from the sample. This type of calibration can be achieved either by decomposing a metal hydride sample with a very well known hydrogen content or by carefully weighing it before and after desorption. It should be remarked that the experimental system allows the determination of a very low number of hydrogen moles, as low as 1×10^{-6} . This limit can be reduced by an order of magnitude by using a deuterated sample because of the lower background partial pressure of deuterium compared to hydrogen in the vacuum chamber. This value is small enough to allow for

quantitative investigations of hydrogenated metal thin films.

In addition to the former calibration, good response times are needed in coupled DSC–MS systems. That means that the time lag between the signal detected by the DSC and that detected by the MS should be small. It is also desirable that the shape of the MS signal accurately reflects decomposition reaction of the sample. Both characteristics, time lag and shape of the MS signal, are taken into account by the response time function of the system [15] which is mainly affected by the flow and type of carrier gas and the geometry of the experimental system. In this work, the response time function has been characterised by injecting in the system, through the sample furnace (hold at constant temperature, 323 K), a small amount of H_2 gas together with the carrier gas. The hydrogen molecules give an endothermic signal in the calorimeter and also are detected in the vacuum chamber by the MS. Typical time lag values of 10 s, which represent a temperature interval of 2 K at normal heating rates, are obtained from such a calibration procedure. In addition, no modification of the MS signal shape when compared to the DSC signal is observed in such measurements.

3. Sample preparation

The MgH_2 samples were prepared in a Sievert's type set-up by the solid–gas reaction method. Magnesium powder from JMC, 99.9% purity, with an initial particle size in the range of 45 μm , as determined by optical microscopy, was used for the experiments. After several activation cycles of hydrogen absorption and desorption,

the sample was homogenised in hydrogen at 603 K and a pressure of ~ 1 MPa. Just after preparation, the sample was kept under Ar to minimise oxidation until the TDS–DSC measurements were accomplished. The hydrogen content of the sample was measured from the pressure drop in a calibrated volume. A H–Mg ratio of $x=1.40\pm 0.05$ was obtained, which indicates an incomplete transformation of magnesium metal in magnesium hydride. In fact, a quantitative analysis of the X-ray diffraction pattern carried out with the Fullprof software [16], shows that the material is composed of two main phases, tetragonal MgH_2 (75 wt%) and hexagonal Mg (17 wt%) together with a small amount of cubic MgO (8 wt%).

4. Results and discussion

Fig. 2 shows desorption spectra obtained at different heating rates (from 10 to 30 K/min) for as-prepared samples with mean particle size of ~ 45 μm . A single desorption peak is observed in Fig. 3 at all heating rates as expected for almost oxide-free MgH_2 samples. The area under the whole desorption curve increases and the peak temperature shifts to higher values when the heating rate increases.

The desorption rate, the time derivative of the reacted fraction, can be generally expressed as follows [17]:

$$\frac{dr}{dt} = k(P,T) \cdot f(r) \quad (1)$$

where r is the reacted fraction, t the time, $k(P,T)$ the

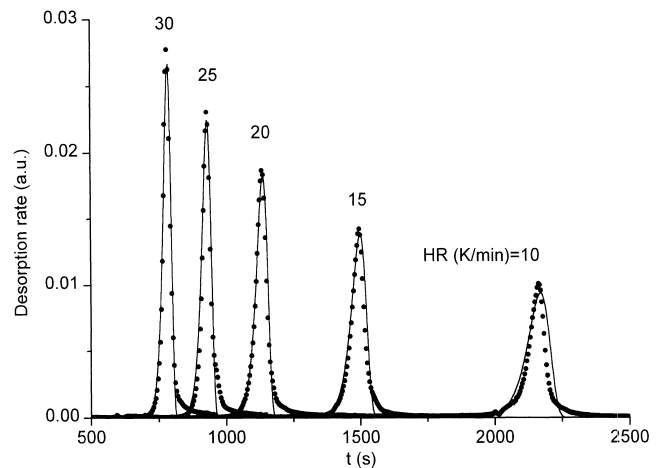


Fig. 3. Desorption rate of MgH_2 samples heated at different heating rates (solid circles), and the corresponding fittings (solid lines), according to a NG mechanism with an exponent $n=4$.

reaction rate, dependent on P, T and sample geometry, and function f dependent on the controlling mechanism.

The temperature dependence of the reaction rate usually follows an Arrhenius type law:

$$k(P,T) = k_0(P) \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where k_0 is pressure dependent pre-exponential factor, E_a the activation energy of the overall reaction and R the gas constant. If a linear temperature heating ramp is imposed on the sample, the term $k(P,T)$ increases with temperature while the term $f(r)$ decreases giving rise to a maximum in

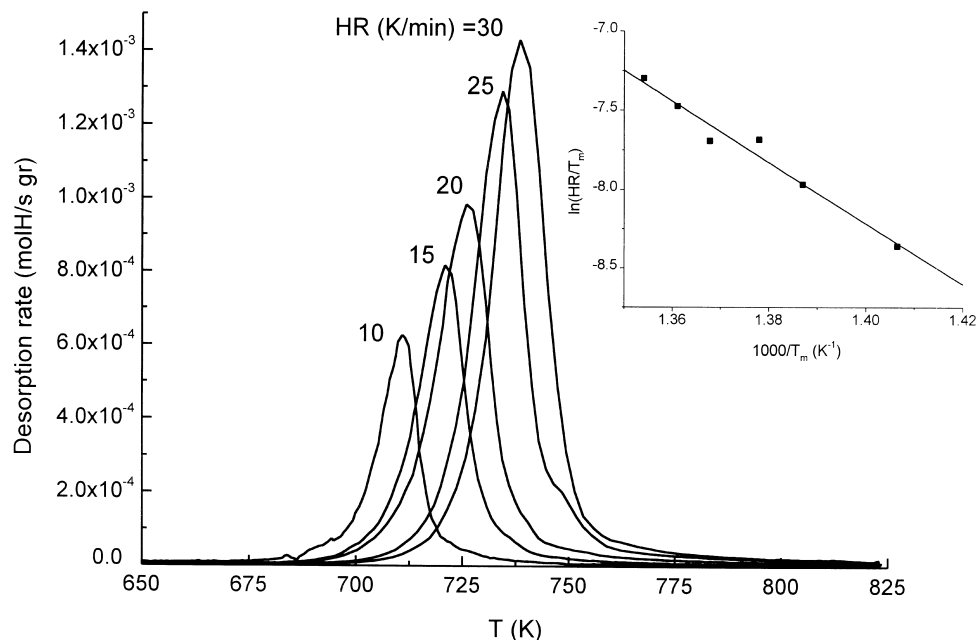


Fig. 2. H-desorption rate curves for MgH_2 at different heating rates. The value of the heating rate is indicated close to each curve. The inset shows an Arrhenius type plot for the $\ln(HR/T_m)$ parameter.

the desorption spectra. Prediction of the position of this peak maximum can be obtained by equating to zero the second time derivative of the reacted fraction. Previous studies have shown that hydrogen desorption from magnesium is controlled by a nucleation and growth (NG) mechanism [18–22]. In this case, the relationship between the reacted fraction and time takes the form:

$$r = 1 - \exp(-(k(P,T)*t)^n) \quad (3)$$

where n is the characteristic exponent of the NG process. From Eq. (3), it can be deduced that the logarithm of the quotient between the peak temperature (T_m) and the heating rate (HR) is linearly related to the inverse peak temperature (T_m^{-1}). The slope of such a plot is proportional to the activation energy of the desorption process. The inset in Fig. 2 corresponds to such an analysis accomplished with data from the desorption peaks in the same figure. A very good linear relationship can be observed. From the slope of the linear fit to the experimental data an activation energy of 161 ± 15 kJ/molH is obtained. This value is in very good agreement with previously published figures which scatter in the range 120–160 kJ/molH [5,19,23–26].

The experimental desorption curves in Fig. 2 should be fitted with the time derivative of Eq. (3), once the temperature dependence of $k(P,T)$ [Eq. (2)] is taken into account. This fitting is presented in Fig. 3 where experimental data correspond to solid circles and continuous lines correspond to the calculated desorption curves. Three free parameters are allowed vary in calculating such curves, the temperature independent pre-exponential factor, k_0 , the activation energy of the overall desorption process, E_a , and the exponent, n . The curves of Fig. 3 were constructed with a k_0 value of $1.8 \times 10^{11} \text{ s}^{-1}$, the same for all the curves, the activation energy was varied from 169 to 162 kJ/molH, with an average value of 166 ± 4 kJ/molH, and the exponent was fixed to $n=4$. The activation energy agrees with that calculated from the temperature peak position method and also with results from the literature. The exponent of the NG process mainly affects the extent of the temperature range in which desorption takes place: the lower the exponent, the wider the desorption peaks. A value of $n=4$ is the best option in order to fit the quite narrow desorption data of Fig. 2.

In a previous investigation on the Mg–H system, it has been shown that desorption follows a NG mechanism with an exponent of $n=2$ [18]. From this value and some additional hypotheses, it was possible to deduce that desorption takes place at a constant nucleation rate and that the growth of the nuclei is controlled by a two-dimensional hydrogen diffusion through the β -MgH₂ phase. That investigation differs from the present one in several important points. Firstly, the desorption process was studied at approximately constant temperatures in the range 570–670 K, much lower than the temperature values of 700–775 K at which the desorption peaks take place in

Fig. 3. Secondly, the hydrogen pressure in those experiments was in the range 0.025–0.60 MPa, much higher than that used in the present experiments. In addition, some surface oxide may have been grown in the samples during the short time they were exposed to air.

The value of the exponent in a NG process depends on several factors. It depends on the growth controlling mechanism (hydrogen diffusion, interface transformation, etc.), on the nucleation rate (constant nucleation, fast nucleation, etc.) and on the growth morphology (one-dimensional, two-dimensional, etc.). In this investigation, we have obtained the same activation energy as in our previous work. Therefore, it seems that the growth controlling mechanism should be the same, i.e. hydrogen diffusion through the β -MgH₂ phase. So the change in the exponent value should be related to the growth morphology or to the nucleation rate. Any difference between the experiments quoted above can be thought of as being responsible for the change in the exponent value. However, we are not able to elucidate at present whether this is a temperature effect, a pressure effect or surface oxidation effects.

5. Conclusions

The desorption spectra of magnesium hydride samples non-exposed to air has been investigated by a combined TDS–DSC technique. They have been analysed with a nucleation and growth model. An activation energy for the H-desorption process of 166 ± 4 kJ/molH has been obtained in very good agreement with previously published results. However, the exponent value obtained in this work, $n=4$, differs from that previously reported, $n=2$. Different possible causes of this discrepancy have been discussed.

Acknowledgements

This work has been supported by Spanish MCYT under contract MAT2001-1260. Technical assistance from F. Moreno is gratefully acknowledged

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