Thermochimica Acta, 103 (1986) 51–56
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

KINETIC STUDIES BY THERMOGRAVIMETRY: THE ROLE OF HEAT TRANSFER OF SAMPLE MASS AND OF SAMPLE HOLDER DESIGN ON METAL HYDRIDE KINETIC RESULTS.

C.BAYANE and N. GERARD

Laboratoire de Réactivité des Solides . LA 23. Faculté des Sciences MIRANDE.
BP. 138. 21004 DIJON cedex. FRANCE.

ABSTRACT

Temperature measurements are carried out , in samples of different masses, according to the function of the material in which the sample holder is machined and as well as the function of its design. Under the same conditions of mass, temperature and hydrogen pressure, the temperature increase inside the sample is changed by a factor of 3 at a temperature of 21°C when the copper crucible is replaced by a plexiglass crucible. In addition , with a sample mass of 10 mg and with the sample holder which gives the best isothermal conditions , the exothermic hydride-formation kinetics are slower than with a less efficient holder or with a larger sample mass

INTRODUCTION

Thermogravimetry is considered as an accurate tool for kinetic studies as the consequence of two points:

a) the possibility of obtaining a well-defined starting period of the reaction
b) the ease of carrying out experiments on small sample masses.

This last point is considered as a way to approach isothermal conditions both in the whole sample and all along the reaction. Any author is convinced of the basic importance of this isothermicity with regards to the reaction because temperature is a very sensitive parameter acting directly on the " driving force"both on the thermodynamic terms of the equilibrium and through the Arrhenius' law, and indirectly, on the precursory stages of adsorption and nucleation. But the claim that the device creates an isothermal surrounding to the sample does not insure that isothermal conditions exist inside the sample all along the reaction. One criterion could be the demonstration of the independence between the reaction rate and a sample parameter as, for instance , its mass.

Such measurements are reported in Fig.1 . They are relative to the hydride formation of $LaNi_5$, according to equation (1).

$$LaNi_5 + 3\ H_2 \rightleftharpoons LaNi_5H_6 \qquad \Delta H_f = -\ 7\ Kcal\ /\ mole.\ H_2 \qquad (1)$$

The equilibrium pressure is 2.5 atmospheres at a temperature of 25 °C.

This hydride formation , moderately exothermic, is carried out near ambiant temperature (21 °C) under a hydrogen pressure of 1 MPa. on an activated sample which consists of quasi-spherical grains , 5µm in diameter, with a specific surface of less than $1m^2$ /g.

Fig.1 shows two curves

i) reaction rate versus sample mass , which consists of two parts separated by a maximum near a mass of 30 mg. On the left of the curve , the reaction rate increases when the mass is increased. On the right , the reaction rate decreases for increasing masses.

ii)Temperature increase (ΔT)in the sample versus sample mass

0040-6031/86/$03.50

A large temperature increase takes place when the mass is changed from 30 mg to 300 mg .

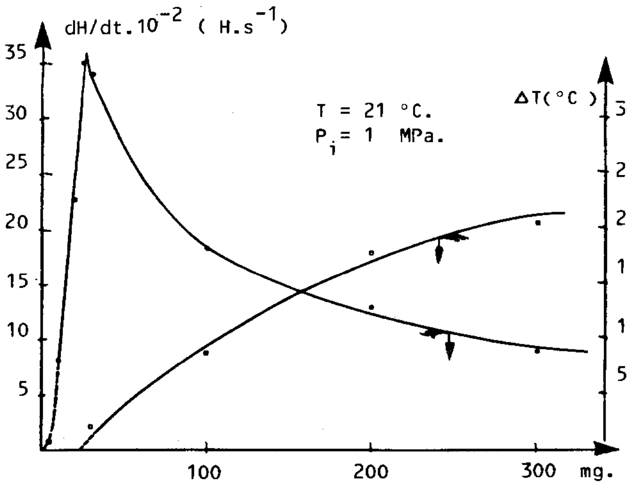

Fig. 1. (●) Reaction rate measured at a transformation ratio of 0.5, versus sample mass. (□) curve of temperature increase versus sample mass.

The attempts to explain these results on the basis of temperature corrections do not succeed in obtaining a corrected reaction rate independent of the mass of the sample (2). Therefore this paper reports the results of an investigation on kinetic changes , of the above reaction , which could be induced by local changes in the sample temperature. These local changes are obtained by modifying the heat transfer function of the sample holder with all other conditions being maintained identical.

EXPERIMENTAL PROCEDURE

Experiments are carried out with either the small mass of 10 mg or the larger mass of 200 mg (to bracket the maximum of the curve of Fig.1). The sample holders, as shown in Fig.2, are cylindrical flat bottom cups 0.5 mm thick, 5 mm deep, with two possible diameters of 10 mm and 5 mm. (which gives a powder bed twice thicker). The sample holders are machined from materials of different specific heat conductivity, such as plexiglass, stainless steel or copper. in addition , the copper holder has the special design shown in Fig.2 which consists of a large lateral surface which insures a maximum heat exchange with the gas.

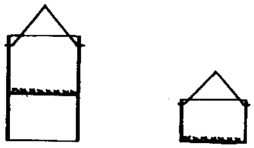

Fig.2 . Diagram, cross section of two types of sample holders.

EXPERIMENTAL RESULTS

Relationship between the reaction rate and the temperature increase (ΔT)

ΔT is defined as the increase in temperature resulting from the reaction by reference to the imposed temperature ($\Delta T = T - T_i$). Fig.3 represents by straight lines the change in ΔT versus the hydrogen pressure. The changes are the result of the same reaction, with a mass of 200 mg, but this reaction is obtained by using sample holders of different size, built in different materials or using different arrangements : the sample is covered either with silica wool or with silver wool, and in one case, steel balls are added in the powder bed.

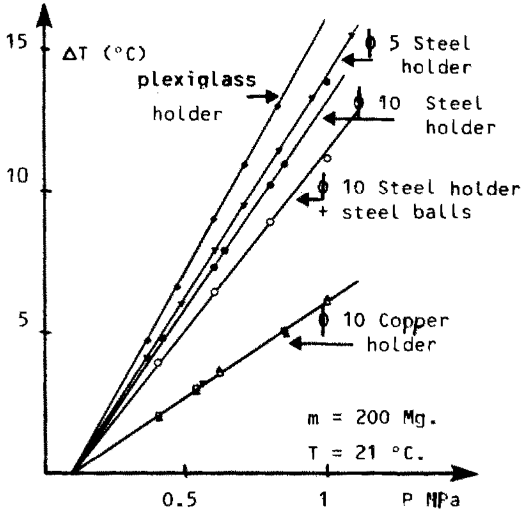

Fig. 3 Temperature increase inside the sample vs. H_2 pressure.

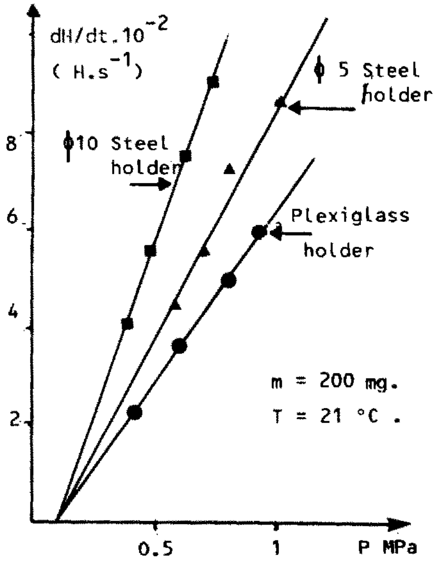

Fig.4 Reaction rate vs. hydrogen pressure

In agreemnt with what could be predicted , ΔT is bigger
i) with a steel holder of diameter 5mm than with a steel holder of 10 mm.
ii) with a plexiglass holder than with a metallic holder.
It can be noted that the addition of steel balls is less efficient than the use of a holder with a high specific condictivity, as is the case of the copper holder. In Fig.4 where the reaction rates obtained for the same reaction, as functions of the sample holder properties are compared, it appears that the smaller the temperature increase (steel holder), the faster the reaction rate.

Role of the sample holder properties on the shape of the formation curves.

Fig.5 shows two families of curves, established according to the function of time.
i) the formation curves : $n= f(t)$.
ii) the temperature change during the formation reaction: $\Delta T=f(t)$.
One pair of these curves is obtained with the steel holder , the other pair,with the plexiglass holder. In the two cases, the maximum in the ΔT curves coincides with the inflexion point of the sigmoïd formation curves. But with the steel holder , this inflexion point is obtained near a transformation ratio α=0.5 (ie. 3 H fixed over 6). On the contrary, with the plexiglass holder the inflexion point is shifted towards a transformation ratio of about 0.I which means that , after a shorter nucleation stage, the second part of the reaction is under control of a different elementary step.

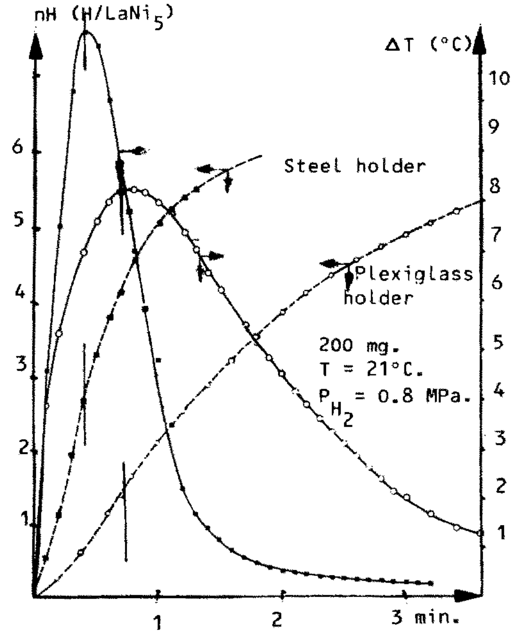

Fig. 5 Formation curves: hydrogen fixed vs. time (dotted lines). Temperature increase vs. time. One family (o)is obtained with the plexiglass holder; the other family (●), with the steel holder.

Interaction sample mass, specific heat conduction of the sample holder.

In this paragraph , the results obtained with two sample masses either of 10 or of 200 mg are exposed. They concern experiments carried out under the same conditions of Pressure and T. but with two holders , one of steel and the other of copper. Fig.6 shows the families of formation curves obtained with samples of 10 mg. Rather surprisingly, the copper holder gives the slowest reaction, with a well-developed first nucleation part whose rate is slower than that corresponding to the homologous part of the curves given by the steel holder. The larger temperature increase developed in the steel holder favours a faster nucleation rate.Fig.7 is relative to reactions carried out with samples of 200 mg. The reactions obtained with the copper crucible are faster than those carried out with the steel crucible. Once again the first part of the sigmoïd , which represents the nucleation stage,is slower with the high efficiency heat exchanger copper holder than with the steel one, but in that case the global reaction remains faster as a consequence of a faster second stage which follows the nucleation stage. One explanation of this apparently complicated result could be (as developed in the case of MgH_2 formations, by ref.3) of a surface coverage associated with a fast nucleation , which is followed by a slow diffusion process

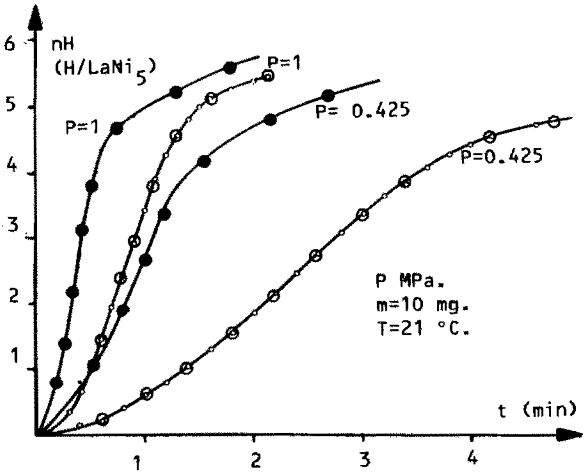

Fig.6 Formation curves. mass of 10 mg.(●) steel holder.(o) copper holder

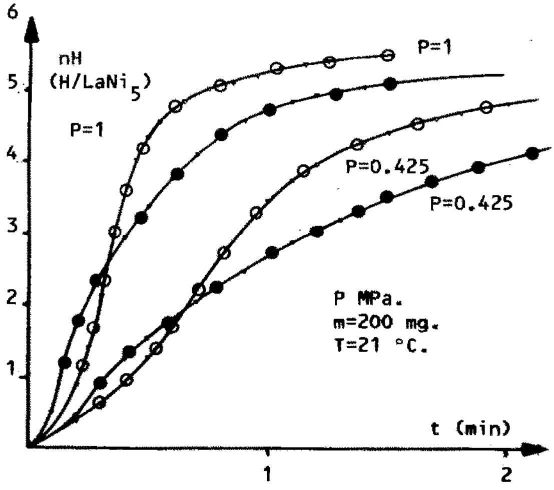

Fig.7 Formation curves. mass of 200 mg. (●) steel holder. (o) copper holder

Pressure dependence as a function of sample mass and of properties of the sample holder.

The pressure dependence corresponds to the equation : $V_{0.5} = f(P_{H_2})$. $V_{0.5}$ is the reaction rate determined from the slope of the formation curves at a given transformation fraction (for instance 0.5). With a mass of 10 mg. these functions are represented by straight lines with both the copper and the steel crucibles. on the contrary, with a mass of 200 mg.the steel crucible gives a linear P dependence whereas with the copper holder the P dependence is expressed as a function of $(P_{H_2})^2$. This last result demonstrates that temperature variations , which affect the nucleation stage, transform the regulating step.

DISSCUSSION.

The first point is that the reaction induces a heat accumulation which creates a temperature increase in the sample. This temperature increase depends on the heat conductivity of the sample holder and on its heat transfer function to the gas. A correlation between the temperature increase and the reaction rate is not simple, as shown by the previous results. But, at least, it can be noted that: a slower nucleation stage corresponds to a reduced temperature increase. This last result can be a consequence of either a smaller number of nuclei per specific area or of a slower growth rate. The change in this initial step of the reaction is at the origin of the change in the P dependence and in the perturbations in the reaction rate.

REFERENCES

1 L. Belkbir, PhD Thesis. Contribution à l'étude cinétique de l'évolution des systemes constitués par l'hydrogene et les alliages de lanthane-nickel faiblement substitués. Dijon . France. July 25 (1979).
2 C.Bayane and N.Gerard J. Less common Met. I07 (I985) 213-219