

previously masked (for example, the 571.8 nm line). In figure 4(c) we present the 'phase' spectrum. All spectra were recorded at the same chopper frequency (1010 Hz). This frequency is situated close to the maximum of the curve from figure 3. The measurements were performed with the system presented in figure 2, the lock-in amplifier working, for the spectra presented in figures 4(a) and (b), in the normal mode.

5 Conclusions

As outlined in the introduction, this method, based on a conventional experimental arrangement, allows firstly the determination of the modulation frequency range for which the separation between two lines (or groups of lines) is a maximum in a chronospectroscopic measurement, without previous knowledge of the lifetimes of the lines. Secondly, in the phase spectra, the fluorescent lines originating from the same metastable level could be easily identified (for example, in figure 4(c) the lines at about 548.5, 571.8, 596.0 and 623.0 nm belong to the same fluorescent series). This method, though stationary, uses the information contained in the lifetime of the luminescent centres. From a more general point of view, it can be considered as complementary to pulsed time-resolved spectroscopy.

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High-accuracy volumetric device for hydrogen sorption kinetic studies

N Gérard, L Belkhir and E Joly

Laboratoire de Recherches sur la Réactivité des Solides, associé au CNRS, Faculté des Sciences Mirande, BP 138, 21004 Dijon Cedex, France

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Abstract This note describes a set-up designed to study heterogeneous solid-gas kinetics, especially hydrogen sorption by intermetallic compounds of high mass formulae such as LaNi_5 . Results for this system are given as examples.

1 Introduction

Kinetic studies of solid-gas systems, in which the mass of the solid is large compared to that of the absorbed gas, cannot be studied by classical thermogravimetric methods, especially for metals or alloys such as Fe-Ti, Zr-Ni, LaNi_5 and hydrogen gas. For such studies we have developed a volumetric set-up in which the main characteristic is that hydrogen amounts fixed or released during the reaction are measured as volume variations of the cell containing the sample. The accuracy of measuring the volume variation (1 mm³ of gas under standard conditions) is such that it allows the use of samples not exceeding 5 mg. Microcrystals of the sample are set in a single layer to minimise self-heating or cooling and gas diffusion through the reacting bed.

Another important point is that temperature must be regulated to better than 0.05 K and pressure maintained strictly constant (with an accuracy greater than 130 Pa (≈ 1 mmHg)) since small variations in these parameters induce appreciable changes in the equilibrium points of these systems.

2 Experimental device

Experimental conditions are 0–100°C and 0–1.5 MPa. The set-up is shown in figure 1. All parts are made of stainless steel; the gas pipes, 3.2 mm in diameter, are connected with Gyro-lock fittings. High-temperature Hocke bellows-sealed valves are used. The sensitive part of the device consists of a differential pressure gauge (with a maximum accuracy of 13 mPa

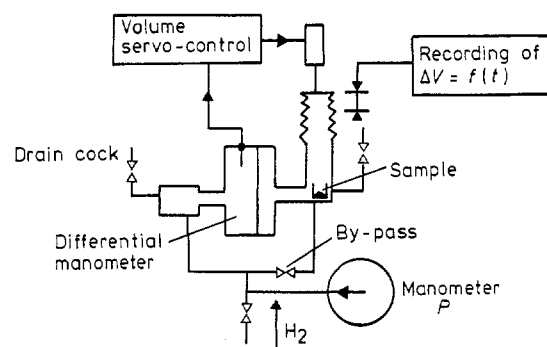


Figure 1 Diagram of the set-up.

Apparatus and techniques

(10^{-4} mmHg)) which operates between a reference chamber and the sample chamber. The reference chamber, 70 cm^3 in volume, is directly fixed to the body of the capacitor-type gauge (Atlas MMM), which is fitted with a 0.01 m^2 stainless steel membrane, the parts of which are assembled with silver rings. The 70 cm^3 measuring chamber contains the sample in a 20 mm plate covered with silica wool to prevent the projection of sample fragments during the reactions.

Standardisation has shown that the bellows volume is in proportion to the length and depends on the position of the free end. This length is determined by a micro-screw with an accuracy of 0.01 mm . Rotation of the screw depends on a variable-speed, two-directional, Brion-Leroux electric motor which is governed by a transducer through an amplifier chain shown in figure 2.

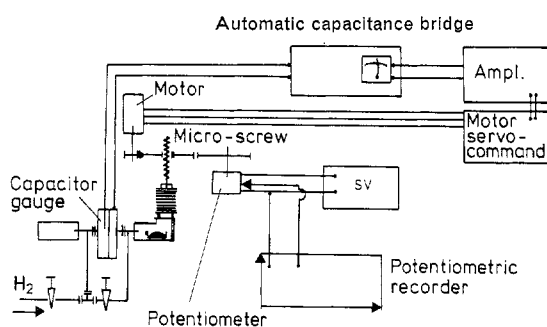


Figure 2 Diagram of the automatic volume control diagram. sv, stabilised voltage.

Rotations of the screw, i.e. volume variations, are transformed into recorded voltage variations by a 10-revolution potentiometer, which rotates simultaneously with the screw. Absolute hydrogen pressure is measured by a Bourdon-type manometer. The whole device is immersed in a thermo-regulated bath, consisting of 30 l of Gilotherm (a dielectric liquid to prevent electric perturbations of the transducer). The temperature of the bath is maintained constant with special care to prevent temperature gradients which could induce pressure variations between the reference and measuring chambers.

3 Procedure

The sample having been put in position, a vacuum is created, and then the hydrogen pressure required for one experiment is simultaneously established in the two chambers which communicate through a by-pass valve. Pressure can be established in less than 20 s. As soon as the valve has been closed, the reaction induces a pressure variation between the two chambers. This variation is detected and automatically compensated by a volume variation of the bellows. The volume variation, recorded as a function of time, after standardisation, gives curves of composition as a function of time, for constant T and P_H .

Example

Formation kinetics of $\text{LaNi}_{4.84}\text{Cu}_{0.06}\text{H}_x$ as a function of hydrogen pressure.

$$P_H = 1.3 \times 10^5 \text{ Pa (1000 mmHg)}, T = 291 \text{ K.}$$

Figure 3 shows a family of curves of composition as a function of time, obtained from a sample activated by twenty formation-decomposition cycles, for hydrogen pressures ranging

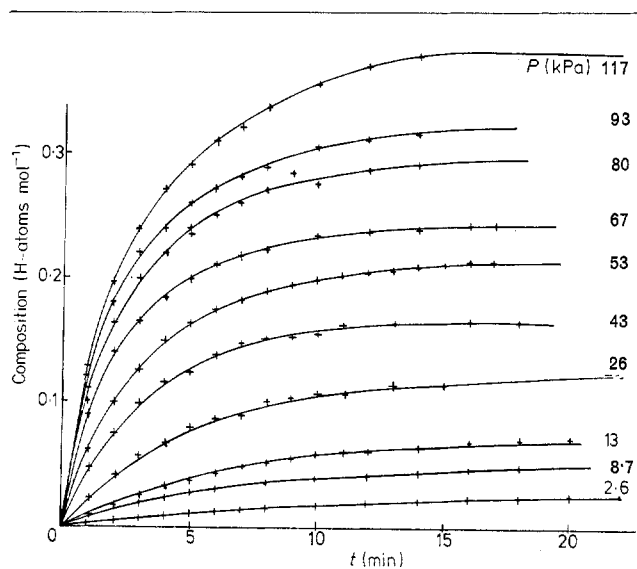


Figure 3 Family of curves of composition as a function of time for $\text{LaNi}_{4.84}\text{Cu}_{0.06}\text{H}_x$ for different hydrogen pressures ($T = 291\text{ K}$).

from 2.6 to 114 kPa (20 to 880 mmHg). Each of these continuously decreasing curves ends on a plateau which corresponds to one x value of the $\text{LaNi}_{4.84}\text{H}_x$ α phase (i.e. insertion of a solid solution of hydrogen in the alloy lattice) for a particular P_H value. From these x values is obtained the isotherm of composition as a function of P_H which gives the area where the α phase exists. The experimental curves of figure 3 can be expressed by $\alpha = f(t)$ with $\alpha = x/x_\infty$. Such curves can be superimposed in an affinity relative to time; this affinity shows that the same process regulates the reaction in these pressure limits. The curves become linear when they are expressed by the equation $-\lg(1 - \alpha) = Kt$. This equation has been given by Adda and Philibert (1966) as a solution of the second Fick equation when the regulating process of the whole reaction is gas diffusion under variable working conditions.

Reference

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