ESTIMATION OF EQUILIBRIUM HYDROGEN PRESSURE - A NEW METHOD

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Abstract

A new method is proposed to estimation of hydrogen pressure in equilibrium with hydride phase in a hydrogen storage material. It is applicable both for hydrogen absorption and desorption in cases where the hydride phase is formed by nucleation and growth mechanism. The proposed method saves considerably the experimental time replacing the conventional time consuming measurement of pressure-composition isotherms, the so called PCT curves. The proposed evaluation procedure is illustrated using hydrogen chemi-sorption at temperatures 623 K, 573 K and 523 K in chosen hydrogen storage alloys Mg-Si-C, Mg-Li-C and Mg-Na-C.

Keywords: Hydrogen storage, magnesium, new method

1. INTRODUCTION

The value of hydrogen pressure in equilibrium with hydrided phase, p_{eq}, defines the stability of respective hydride phase described by its average chemical composition and temperature. At hydrogen pressure above the p_{eq}, the hydride phase β is stable, below the p_{eq}, the hydrogen co-exists with the de-hydride phase α. Typical PCT curve is shown in **Figure 1**.

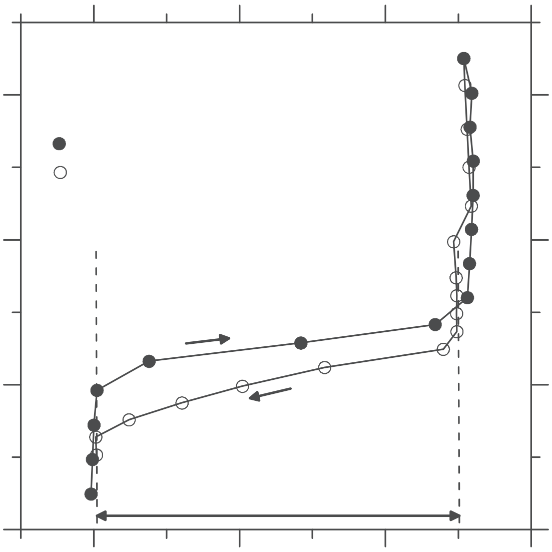

Figure 1 Typical PCT isotherm

After solution of hydrogen in the hydrogen-free material (phase α), the hydride phase is nucleated (interface α/α+β), which grows (α+β plateau) up to the end of α to β transformation. Further increase of hydrogen pressure leads to its solution in β. The pressure p_{eq} is taken from pressure-composition isotherms, the so called PCT curves, as a value of *p somewhere in the middle of the plateau* [1]. In **Figure 1** hysteresis can also be seen that causes the difference in p_{eq}^A observed for absorption and p_{eq}^D for desorption. The plateau slope is not necessary constant over the whole length of the plateau and can differ in absorption a desorption branches. The major cause of the slope is usually attributed to compositional inhomogenities. The variation of pressure p over the plateau should be understood as an uncertainty of obtained p_{eq}. In reality, the PCT curve is very sensitive also to equilibration of the system and the measurement must be - especially at the both ends of the plateau, where β starts to nucleate and/or β starts to decompose - conducted very slowly. The experimental time needed to estimation of p_{eq} can be reduced using kinetic measurements and new evaluation method proposed in the present paper.

2. EXPERIMENTAL

Samples were prepared from pure Mg (3N8), Mg_2Si prepared by mechanical alloying from Mg and pure Si (6N) and from pure powders of LiF, NaF (purchased from Sigma Aldrich). The sample composition was modified by carbon black (CB) with O_2 < 2 wt.%, S < 0.17 wt.% purchased from CABOT EMEA. The samples are labeled hereafter as S (Mg-10Mg$_2$Si-14CB - all in wt. %), L (Mg-13LiF-13CB) and N (Mg-13NaF-13CB). Samples were prepared by ball milling (BM) in hydrogen atmosphere using Fritsch Pulverisette6 ball-mill. The mass ratio of the milling balls to the milled blend was about 60 and the milling cycle - 10 min milling/50 min cooling - was repeated 20 times. Hydrogen sorption experiments were carried out using Sieverts-type gas sorption analyzer PCT-Pro Setaram Instrumentation at constant temperatures 523, 573 K and 623 K and under several values of pressure p below (desorption) and/or above (absorption) the presumed value of p_{eq}. The purity of both hydrogen and helium (calibration gas) was 6N. All manipulations of the milled powder were done in the glove box in protective Ar atmosphere. For more details on the experimental procedure - see in [2].

3. RESULTS

The measurement was conducted with sample S in both absorption and desorption mode at temperatures 623 K and at 573 K, in absorption mode at 523 K and with samples L and N in desorption mode at 623 K. Examples of measured kinetic curves (time dependence of fraction $f = c_H/c_H^{max}$; c_H - hydrogen concentration, c_H^{max} - maximum hydrogen concentration) are shown for sample S in **Figure 2**. The examples document that all the curves were sigmoid-type, which implied that the sorption occured by nucleation and growth mechanism. This is more evident in **Figures 3a, b**, where the same curves, plotted in co-ordinates $[-\ln(1-f)]^n$, are well linear [3].

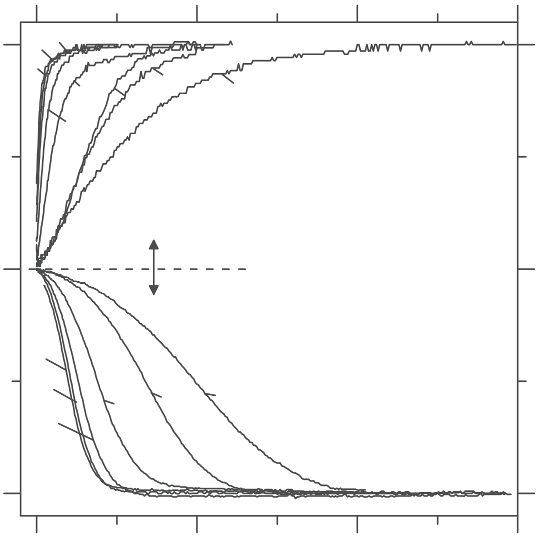

Figure 2 Examples of measured kinetic curves [2], sample S, T = 623 K

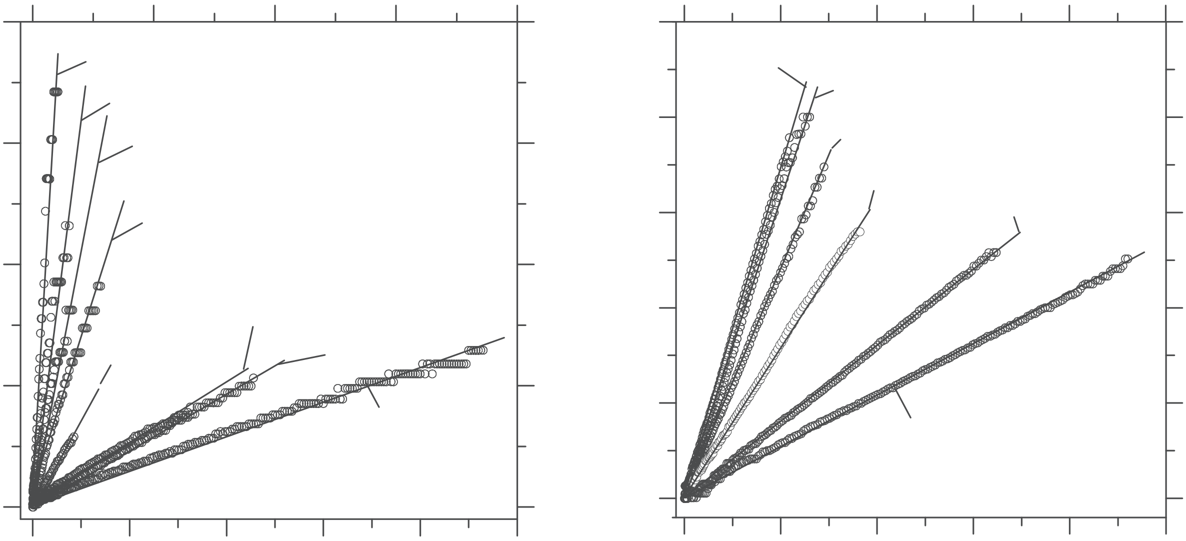

Figure 3 Kinetic curves from **Figure 2** linearized, a - absorption, b - desorption

4. THEORY - EVALUATION OF DATA

We propose to describe the absorption process by a cascade (sequence) of nucleation and growth and the desorption process as hydride decay and its gradual decomposition. The both sorption processes can be schematically presented as a cascade of two bound partial processes with rate constants k_i that depend on temperature

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \quad . \tag{1}$$

The transformation rate can be quantified by time derivative $y = (df/dt)$ that depends on time t itself, on temperature T and on driving force, which is a function of departure of instantaneous hydrogen pressure from unknown equilibrium pressure $|p(t) - p_{eq}|$. Since the sorption was measured at constant temperature, T can be considered as a fixed parameter.

The description can be further simplified by fixing the time variable t: We consider a simple theory describing the cascade that does not involve the final state - i.e. the state approaching the end of transformation (saturation of the sample by reaction product by absorption or total de-hydrogenation by desorption). In other words, the relation for y does not contain any multiplication factor involving $(1-f)$ for absorption and/or f for desorption. This can be satisfied, when we examine y in time sufficiently far from final state of transformation (1). We propose the inflexion point t_i of $f(t)$, which is a well-defined time, when the rate of nucleation and growing is *approximately* balanced and, at the same time, no *other constraints are in effect significantly*. In this way, the time variable can be also fixed and y can be considered only as a function of pressure. In **Figure 4a**, a typical example of kinetic curve is shown. The same curve plotted in co-ordinates $[-\ln(1-f)]^n$ vs desorption time (**Figure 4b)** becomes linear in region, where the nucleation and growing mechanism operates [3].

It can be seen that the inflexion point t_i is well inside the linear part (**Figure 4c**). Nonlinear tail indicates the influence of terms inhibiting the sorption due to exhausting the hydride phase. The nucleation and growth mechanism in samples L and N operated up to about $f = 0.6$ (for sample N, desorption at 623 K - see **Figure 4b**), in sample S typically up to about $|f| = 0.9$ (**Figures 3 a, b**).

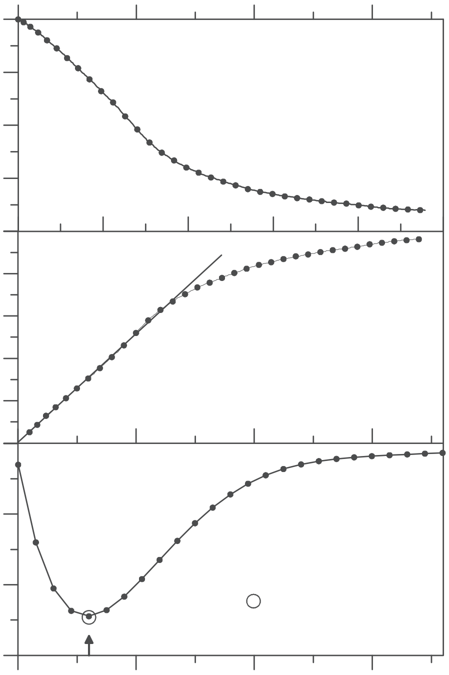

Figure 4 Example of kinetic curve *f* (a), linearized *f* (b) and time derivative of *f* (c)

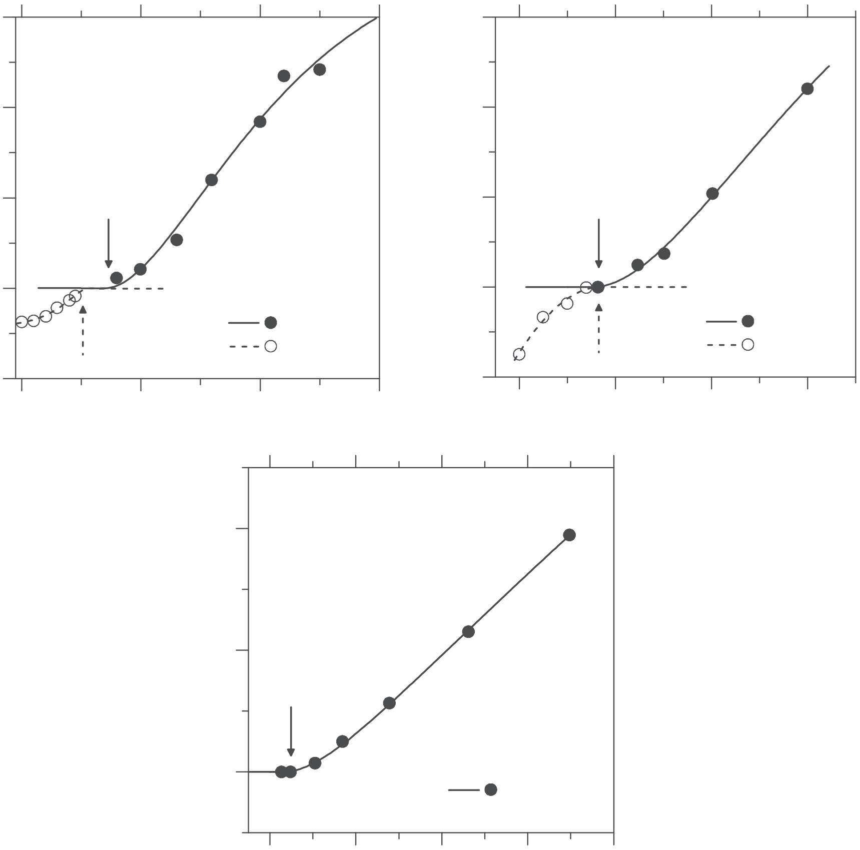

Figure 5 Points - time derivative of *f* in inflexion t_i, lines - fit of **Equation (2)**, sample S a - 623 K, b - 573 K, c - 523 K

Values of maximum first derivative $y(p) = (\mathrm{d}f / \mathrm{d}t)_{max}$ are plotted if **Figures 5a, b** and **Figure 6** in dependence on hydrogen pressure p. They were fitted by *Cascade function* [4]

$$y(p) = k_3 \left\{ 1 + \frac{k_1 \exp\left[-k_2 \mid p - p_{eq} \mid\right] - k_2 \exp\left[-k_1 \mid p - p_{eq} \mid\right]}{k_2 - k_1} \right\}, \tag{2}$$

with four fitting parameters: k_1, k_2, k_3 and p_{eq}. Following constraints must be assured: $p \geq p_{eq}$ for absorption and $p \leq p_{eq}$ for desorption and $k_1 \neq k_2 > 0$. The function $y(p)$ varies from 0 at $p = p_{eq}$ to k_3 at $p >> p_{eq}$.

Values of equilibrium hydrogen pressure obtained by measurements of pressure-composition isotherms (PCT) and by the method proposed in the present paper are listed in **Table 1**.

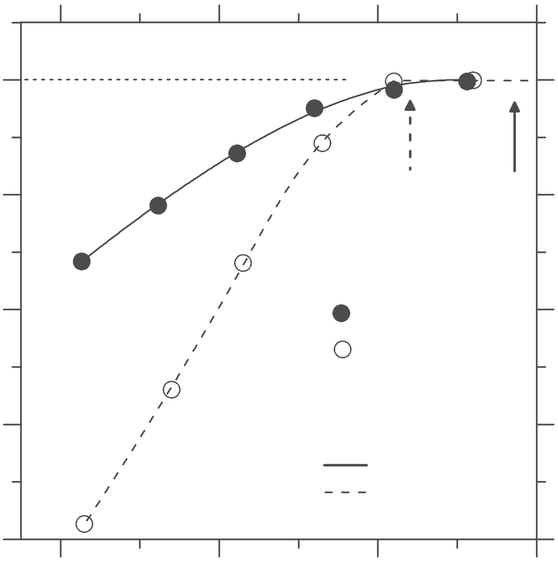

Figure 6 Points - time derivative of f in inflexion t_i, lines - fit of **Equation (2)**. Samples L and F, 623 K.

Table 1 Comparison of values of equilibrium hydrogen pressure obtained by measurements of pressure-composition isotherms and by the proposed method

Sample	*T* (K)	absorption / desorption	Conventional technique (from PCT) (MPa)	New method (MPa)
S	623	p_{eq}^{A}	0.8 ± 0.1	0.7 ± 0.2
		p_{eq}^{D}	0.57 ± 0.05	0.6 ± 0.2
	573	p_{eq}^{A}	0.20 ± 0.05	0.15 ± 0.05
		p_{eq}^{D}	0.10 ± 0.05	0.17 ± 0.05
	523	p_{eq}^{A}	0.04 ± 0.01	0.03 ± 0.02
L	623	p_{eq}^{D}	0.58 ± 0.05	0.5 ± 0.6
N	623	p_{eq}^{D}	0.4 ± 0.1	0.43 ± 0.01

5. SUMMARY

New method was proposed enabling the estimation of equilibrium hydrogen pressure above a hydride phase of hydrogen storage alloy p_{eq}. The strength of the new evaluation procedure was tested for both absorption and desorption in chosen Mg-based alloys in temperature interval from 523 K to 623 K. Values of p_{eq} obtained by both procedures agree well within the experimental errors.

ACKNOWLEDGEMENTS

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