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EVALUATION OF METAL HYDRIDE THERMOGRAMS BY A DIFFERENTIAL-CORRECTION TECHNIQUE

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ABSTRACT

A least-squares linear-Taylor differential-correction technique has been used for the rapid evaluation of thermogravimetric curves obtained during the decomposition of magnesium hydride, iron–titanium hydride and lanthanum–nickel hydride. For magnesium hydride and iron–titanium hydride the Avrami–Erofe'ev equation fits the experimental data, thus indicating that nucleation is the rate-determining step under thermogravimetric conditions. For lanthanum–nickel hydride a combination of the Avrami–Erofe'ev equation and the phase boundary movement equation fits the data up to a fractional decomposition of 0.8. For magnesium hydride decomposition the activation energy E and the pre-exponential factor Z are dependent on the hydrogen pressure ($E = 101.2$ kJ mole^{-1} and $Z = 8.96 \times 10^7$ at 0.30 MPa, while $E = 66.3$ kJ mole^{-1} and $Z = 4.77 \times 10^7$ at 0.11 MPa). For iron–titanium hydride ($E = 28.4$ kJ mole^{-1}) and lanthanum–nickel hydride ($E = 13.4$ kJ mole^{-1}) the values are independent of pressure.

INTRODUCTION

The use of thermogravimetric methods at high pressures yields rapid preliminary kinetic data on the decomposition of compounds.

Doyle[1] has shown that the equation of a thermogravimetric curve is given by

$$g(\alpha) = \frac{ZE}{Rq}\left[\frac{e^{-x}}{x} - \int_{x}^{\infty} \frac{e^{-u}}{u}\,du\right] \tag{1}$$

where Z is the pre-exponential factor, E the activation energy, R the gas constant and q the heating rate. $g(\alpha)$, a function of the fractional decomposition α, describes the mechanism of the decomposition, $u = E/RT$ and $x = E/RT_\alpha$, where T is the temperature and T_α the temperature at fractional decomposition α.

If the experimental data can be fitted to eqn. (1) the probable mechanism of the reaction as well as values of Z and E can be found. To do this it is necessary to integrate the exponential integral and Doyle[1], Horowitz and Metzger[2] and Zsakó[3] have discussed approximate methods for this purpose. In addition, Šatava and Škvara[4] and Ozawa[5] have devised graphic methods for obtaining a solution but in our experience the values of E and Z obtained by these methods are only approximate. In the present study a least-squares linear-Taylor differential-correction technique[6] was used to fit experimental data obtained from the thermogravimetric decomposition curves of magnesium hydride, iron–titanium hydride and lanthanum–nickel hydride, to eqn. (1). Accurate values of Z and E can be found by this method.

METHOD OF CALCULATION

In the differential correction technique estimates, Z^0 and E^0, of Z and E are made. These, together with experimental values of α and T, are used to calculate residuals

$$R_i = \frac{Z^0E^0}{Rq}\left[\frac{e^{-x_i}}{x_i} - \int_{x_i}^{\infty} \frac{e^{-u}}{u}\,du\right] - g(\alpha_i)$$

The residuals are then used to construct the normal equations which can be written in matrix form, viz.

$$\begin{bmatrix} \sum_i \left(\frac{\partial g(\alpha_i)}{\partial Z}\right)^2 & \sum_i \left(\frac{\partial g(\alpha_i)}{\partial Z}\right)\left(\frac{\partial g(\alpha_i)}{\partial E}\right) \\ \sum_i \left(\frac{\partial g(\alpha_i)}{\partial Z}\right)\left(\frac{\partial g(\alpha_i)}{\partial E}\right) & \sum_i \left(\frac{\partial g(\alpha_i)}{\partial E}\right)^2 \end{bmatrix} \begin{bmatrix} \delta Z \\ \delta E \end{bmatrix} = \begin{bmatrix} -\sum_i \frac{\partial g(\alpha_i)}{\partial Z} R_i \\ -\sum_i \frac{\partial g(\alpha_i)}{\partial E} R_i \end{bmatrix}$$

Solution of the matrix equation gives the differential correction (δZ δE). Improved estimates Z' and E' are obtained by adding these differential corrections to the previous estimates Z^0 and E^0. The entire procedure can be repeated until sufficiently accurate values of Z and E are obtained.

The partial derivatives may be obtained in either of two ways. The right-hand side of eqn. (1) can be written as an asymptotic series in $x = E/RT$ to give

$$g(\alpha) = \frac{ZT}{q} e^{-E/RT} \sum_{n=1}^{\infty} (-1)^{n+1}\, n!(RT)^n E^{-n}$$

Differentiation with respect to Z and E leads to

$$\frac{\partial g(\alpha)}{\partial Z} = \frac{T}{q} e^{-E/RT} \sum_{n=1}^{\infty} (-1)^{n+1}\, n!(RT)^n E^{-n}$$

and

$$\frac{\partial g(\alpha)}{\partial E} = \frac{ZT}{q} e^{-E/RT} \left[\sum_{n=1}^{\infty} (-1)^n \cdot n \cdot n!(RT)^n E^{-(n+1)} - \sum_{n=1}^{\infty} (-1)^{n+1}\, n!(RT)^{n-1} E^{-n}\right]$$

The above series converge rapidly for values of $x > 10$.

Alternatively, a rational approximation[7] may be used for the right-hand side of eqn. (1), viz.

$$g(\alpha) = \frac{ZE}{Rq}\frac{e^{-x}}{x}\left[1 - \frac{x^4 + a_1x^3 + a_2x^2 + a_3x + a_4}{x^4 + b_1x^3 + b_2x^2 + b_3x + b_4}\right]$$

where,

$a_1 = 8.5733287401$, $b_1 = 9.5733223454$,
$a_2 = 18.0590169730$, $b_2 = 25.6329561486$,
$a_3 = 8.6347608925$, $b_3 = 21.0996530827$,
$a_4 = 0.2677737343$, $b_4 = 3.9584969228$.

For $1 \leq x \leq \infty$ the error in the above approximation is less than

$$2 \times 10^{-8}\frac{ZE}{Rq}\frac{e^{-x}}{x}$$

The rational approximation can easily be differentiated to give the required partial derivatives.

The analytical form of the function g(α) depends on the mechanism of the decomposition. Jacobs and Tomkins[8] discuss a large number of cases but we have found that many decomposition reactions can be described by either the Avrami–Erofe'ev[9–12] equation

$$g_1(\alpha) = (-\ln(1-\alpha))^{1/n} = kt \tag{2}$$

or the phase boundary movement equation

$$g_2(\alpha) = 1 - (1-\alpha)^{1/n} = k't \tag{3}$$

where $n = 2$ or 3, k and k' are rate constants and t is the time. For the decomposition of magnesium hydride it has previously[13] been found that eqn. (2) describes the kinetics well at temperatures near the equilibrium dissociation temperature, while eqn. (3) describes the kinetics well at other temperatures. In many thermogravimetric determinations the temperature at any time does not differ much from the equilibrium decomposition temperature and the function $g_1(\alpha)$ should then be used in eqn. (1).

For some reactions a combination of mechanisms occurs. For these $g_1(\alpha)$ and $g_2(\alpha)$ may be combined to give

$$g_3(\alpha) = (1-\alpha)(-\ln(1-\alpha)^{1/2}) + \alpha(1-(1-\alpha)^{1/3})$$

At low values of α the temperature is near the equilibrium dissociation temperature and $g_3(\alpha)$ is then nearly equal to $g_1(\alpha)$. At higher values of α, $g_3(\alpha)$ tends to $g_2(\alpha)$.

EXPERIMENTAL

Magnesium hydride was synthesised as previously[13] described. Both FeTi and $LaNi_5$ were prepared by arc-melting mixtures of the appropriate metals in a watercooled copper crucible using an argon atmosphere. The intermetallic compounds were powdered and screened so that the range of the particle size was between 0.1 and 0.2 mm.

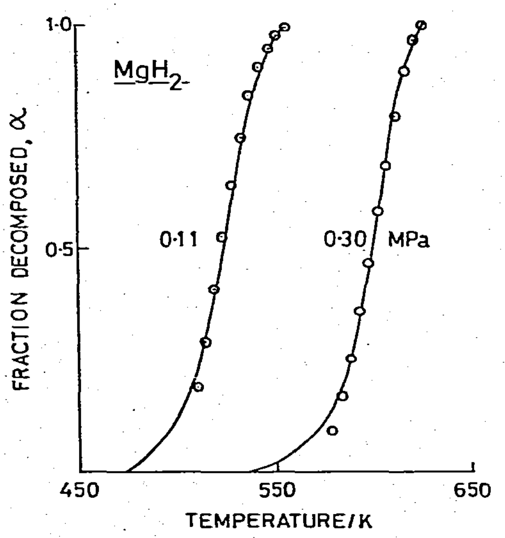
The high pressure microbalance previously described[13] was used to determine the thermograms. Either magnesium hydride or one of the alloys was loaded on to the balance and hydrogen repeatedly absorbed and desorbed so as to stabilize the structure of the metal hydride. After finally saturating the sample with hydrogen, thermograms were obtained in the normal manner using constant heating rates and hydrogen pressures.

The graphic method of Šatava and Škvara[4] was used to obtain the initial estimates Z^0 and E^0.

RESULTS AND DISCUSSION

Figures 1, 2 and 3 show curves obtained for the decomposition of magnesium hydride, iron–titanium hydride and lanthanum–nickel hydride, respectively. These curves were fitted to the experimental points using the kinetic functions and heating rates indicated in Table 1. Shown in Table 2 are the values obtained for the pre-exponential factors, activation energies and means of the squared sums of the final residuals, the means being used as a measure of the goodness of fit.

Since the sum of the squared final residuals is a measure of the consistency between the experimental data and the presumed kinetic function, the present method can be used for the rapid testing of the validity of various kinetic equations. In the present study the functions shown in Table 1 were those that gave the lowest value for $\Sigma_i(R_i(\text{final}))^2$. For both the decomposition of magnesium hydride and iron–titanium hydride the data are consistent with the Avrami–Erofe'ev equation, thus



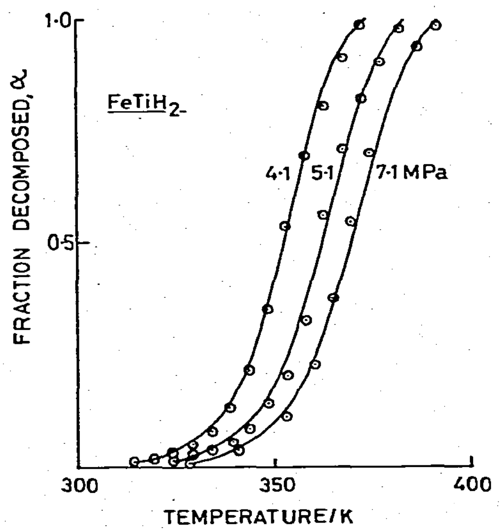


Fig. 1. Fractional decomposition of magnesium hydride vs. temperature.

Fig. 2. Fractional decomposition of iron-titanium hydride vs. temperature.

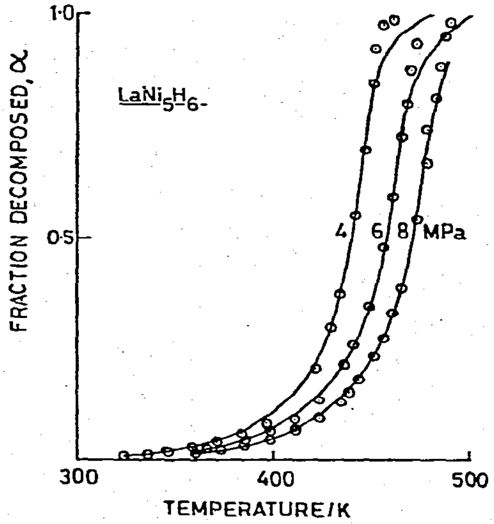


Fig. 3. Fractional decomposition of lanthanum–nickel hydride vs. temperature.

TABLE 1

KINETIC FUNCTIONS AND VALUES OF PARAMETERS FOR THE DECOMPOSITION OF METAL HYDRIDES

Reaction	*g(α)*	*Heating rate (K min⁻¹)*
$MgH_2 = Mg + H_2$	$(-\ln(1-\alpha))^{1/2}$	4.45
$FeTiH_2 = FeTiH + \frac{1}{2}H_2$	$(-\ln(1-\alpha))^{1/3}$	0.88
$LaNiH_6 = LaNi + 3H_2$	$(1-\alpha)(-\ln(1-\alpha))^{1/2} + \alpha(1-(1-\alpha)^{1/3})$	2.05

TABLE 2

PRE-EXPONENTIAL FACTORS, ACTIVATION ENERGIES AND PRECISION OF FITTING FOR HYDRIDE DECOMPOSITION REACTIONS

Reaction	*Pressure (MPa)*	*Pre-exponential factor*	*Activation energy (kJ mole⁻¹)*	$\frac{1}{n}\Sigma_i(R_i(final))^2$
$MgH_2 = Mg + H_2$	0.30	8.96×10^7	101.2	3.39×10^{-4}
	0.11	4.77×10^5	66.3	2.03×10^{-3}
$FeTiH_2 = FeTiH + \frac{1}{2}H_2$	4.14	4.68×10^2	28.8	2.79×10^{-4}
	5.13	4.34×10^2	29.1	4.82×10^{-4}
	7.05	1.87×10^2	27.7	7.13×10^{-4}
$LaNi_5H_6 = LaNi_5 + 3H_2$	4.00	6.80×10^{-1}	14.2	1.41×10^{-4}
	6.00	3.16×10^{-1}	12.6	9.02×10^{-5}
	8.00	3.38×10^{-1}	13.3	2.90×10^{-5}

indicating that slow nucleation plays a role in determining the rate of the reaction.

The free energy change, ΔG_i, accompanying the formation of a particle of product during the decomposition is given by

$$\Delta G_i = n\Delta G_{\mathrm{A}} + su^2\gamma$$

where n is the number of atoms in the particle of metal, ΔG_{A} the bulk-free energy change per molecule for the decomposition reaction, s a shape factor, u a dimension of the particle, and γ the strain energy per unit interface between the product and the undecomposed hydride. It can also be shown[8] that growth of the nuclei only takes place above a critical size of the particle, u_{eq}, given by

$$u_{\mathrm{eq}} = 2V_{\mathrm{m}}s\gamma/(3\Delta G_{\mathrm{A}}s')$$

where V_{m} is the molecular volume of the product. During the decomposition of magnesium hydride the magnesium atoms have to change from a body-centred tetragonal to a hexagonal close-packed configuration in the metal. The strain energy γ is therefore expected to be fairly large. For both experimental pressures the temperature range in which the decomposition takes place is relatively small (60° at 0.30 MPa and 70° at 0.11 MPa) and the temperature at any instant does not differ much from the equilibrium dissociation temperature. ΔG_{A} is therefore relatively small at any instant. The combination of large γ and small G_{A} results in large values of u_{eq}. Growth therefore only occurs after relatively large nuclei have been formed.

The above remarks also apply to iron–titanium hydride where the structure[14] changes from cubic ($\mathrm{FeTiH_{1.93}}$) to tetragonal (FeTiH) and the decomposition also takes place in a small temperature range (about 70°).

For the decomposition of lanthanum–nickel hydride a combination of mechanisms was found to fit the data up to a value of α = ca. 0.8. Both the hydride and the intermetallic compound have hexagonal structures but the unit cell of the hydride is 25% larger than that of the intermetallic compound[15]. The decomposition takes place over a temperature range of about 170° and towards the end of the reaction there is a relatively large difference between the equilibrium dissociation temperature and the experimental temperature. Nucleation is therefore rate-determining at small values of α but phase boundary movement becomes the rate-determining mechanism at higher values of α. The mechanism for values of α above 0.8 is not known.

In the case of magnesium hydride the activation energy is highly dependent on the pressure. It has previously[13] been found that phase boundary movement is the main rate-determining factor at higher pressures and that the rate constant is then a linear function of the pressure. This leads to the conclusion that the mechanism is dependent on the pressure and that nucleation ceases to play a significant role at higher pressures.

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