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Kinetics of hydrogen absorption in the intermetallic $Zr(Al_{0.2}Fe_{0.8})_2$

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Abstract

The hydriding kinetics of $Zr(Al_{0.2}Fe_{0.8})_2$ was studied at four different temperatures between 238 K and room temperature (298 K) and at an approximately constant pressure of 10 atm H_2. This compound is characterized by the largest hydrogen capacity in the $Zr(Al_xFe_{1-x})_2$ intermetallic system, which exhibits an interesting and anomalous hydriding behaviour. The experiments were carried out with thin intermetallic pieces of definite thickness in order to facilitate the data interpretation. Special precautions were taken during the slicing of the brittle compounds. Visual and metallographic examinations of partly hydrogenated compounds imply a contracting envelope type of hydrogenation. A simple mathematical analysis of the time-dependent hydrogen absorption curves yields the interface velocity u of the advancing hydride. The derived values are approximately in the range 10^{-3}–5×10^{-3} mm s^{-1} for the investigated temperatures and pressure. An activation energy of about 0.14 eV (H atom)$^{-1}$ (27 kJ (mol H_2)$^{-1}$) was estimated for the hydrogenation process.

1. Introduction

The $Zr(Al_xFe_{1-x})_2$, $0 \leqslant x \leqslant 1$, system exhibits an interesting and anomalous hydriding behaviour [1]. Small amounts of aluminium ($x \approx 0.1$) substituting iron in $ZrFe_2$, initiate hydrogen absorption, while large quantities of aluminium ($x > 0.75$) inhibit the hydrogen uptake in the intermetallic system. This is not consistent with the monotonic increase in the corresponding hydride stabilities induced by the aluminium additions. The question thus arises as to whether such a behaviour may be related to kinetic rather than thermodynamic effects. In the present work we report the results of a hydrogenation

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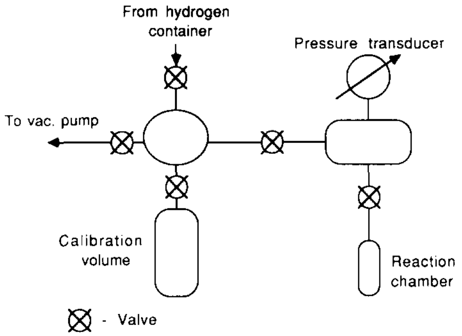
kinetic study of $Zr(Al_{0.2}Fe_{0.8})_2$. This compound is characterized by the largest hydrogen capacity in the $Zr(Al_xFe_{1-x})_2$ system. The research was carried out along the lines of a systematic kinetic approach [2] deduced from extensive work on rare earth and actinide metals. According to this approach the experiments should be performed with samples of definite geometrical form. In addition, the analysis of the kinetic curves, obtained at definite pressure and temperature, should be combined with a visual (metallographic) examination of partially hydrogenated specimens. The purpose of the present research is twofold. First, it examines the significance of kinetic results for massive intermetallic samples which present some experimental difficulties, *e.g.* brittleness, grooves. Secondly, it initiates the kinetic study of one of the interesting hydrogen-absorbing systems. It should be mentioned that this work was partly stimulated by a distinct variation in the nickel cohesion properties in $LaAl_xNi_{5-x}$ intermetallics [3]. The properties of the latter system resemble some of, but not all, the peculiar hydriding features of the $Zr(Al_xFe_{1-x})_2$ compounds.

2. Experimental procedure

$Zr(Al_{0.2}Fe_{0.8})_2$ intermetallic samples were prepared in an arc furnace under an argon atmosphere by melting the weighted fraction of the pure metals on a water-cooled copper hearth. The Laves phase cubic structure of $Zr(Al_{0.2}Fe_{0.8})_2$ ($a = 7.126$ Å) was confirmed by X-ray diffraction. The melted pellets were mounted in "Kold Mount" (a two-components epoxy resin) made by Vernon-Benshoff. Latter we also used an epoxy mount made by Buehler. The mounted samples were cut into thin slices in a wheel saw utilizing wafering blades. The mount kept the brittle samples tight and prevented them from breaking apart into many small pieces. This always occurred on cutting non-mounted intermetallics. The sliced intermetallics were taken off the mount either by slightly pushing them out or by dissolving the mount with acetone. The samples had well-defined thicknesses in the range 0.50–2.00 mm and irregular planar shapes resembling rectangles in most cases. Rectangular dimensions were estimated, when necessary, from the measured planar areas. A substantial effort was put into preparing the specimens in a way warranting reproducible results. The procedure consisted of washing the sliced pieces first by acetone and then by alcohol in an ultrasonic bath. From this stage on any finger contact with the compounds was completely avoided. The samples were subsequently well dried. The sample holder was also cleaned and thoroughly dried before each experiment. The treated $Zr(Al_{0.2}Fe_{0.8})_2$ was then introduced into the hydrogenation system (Fig. 1) and pumped by a diffusion pump for 1.5 h at a temperature of 423 K. The omission of one of these stages usually led to very significant changes in the hydrogenation reaction times, although the overall hydrogen capacity did not deteriorate. The ultimate vacuum at room temperature was in the 10^{-7} Torr range near the diffusion pump and somewhat lower in the reaction



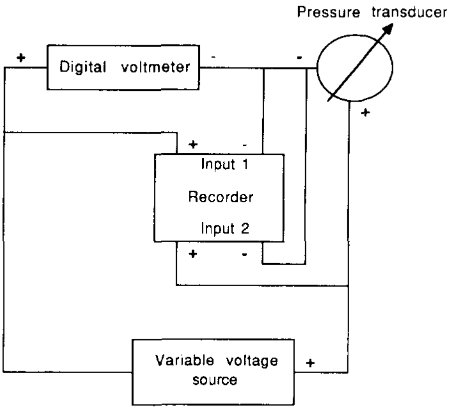


Fig. 1. A schematic representation of the hydrogenation system.

Fig. 2. A block diagram of the pressure measurement circuit.

chamber. The hydriding kinetics of $Zr(Al_{0.2}Fe_{0.8})_2$ was studied at four different temperatures between 238 K and room temperature (298 K), and at an approximately constant pressure of 10 atm H_2. The temperatures were controlled within ± 1 K by a Haake refrigerating facility which circulated a working cooling liquid composed of 40% ethylene glycol and 60% water. It was necessary to maintain approximately a constant pressure during the hydrogenation process in order to have a meaningful analysis of the kinetic data. The experimental set-up was therefore arranged in a way that only a small pressure drop of the order of 0.5 atm was necessary to accomplish the whole hydrogen absorption. Such a small pressure variation was sensitively measured on the full scale of a y–t recorder by utilizing a variable voltage source for appropriate biasing of the output of the pressure transducer (Fig. 2). Some of the samples were partially hydrogenated and then taken out of the experimental system for further examination. This was done by abruptly evacuating the hydrogen gas from the reaction chamber on reaching the desired partial hydrogenation. The sample was "poisoned" by cooling it down to liquid nitrogen temperature before exposing it to the ambient atmosphere. The temperature variation during a complete hydrogenation was followed by a thermocouple located in a specially drilled small hole in the stainless steel reactor near the sample location. A similar experiment was carried out also in a glassware system. In both cases the observed temperature variation was less than 1 °C.

3. Results and analysis

The raw kinetic results are recorded plots of the pressure variation $p(t)$, induced by the hydrogen absorption in the intermetallic compound *vs.* the elapsed time t. It is most convenient [2] to present the time-dependent hydrogen absorption curves in the form of $\alpha(t)$, the reacted fraction of the metal, *vs.* t. Such a presentation normalizes the results for samples of different sizes and weights and enables a geometrical analysis. $\alpha(t)$ is obtained in a straightforward way from the ratios $\Delta p(t)/\Delta p_{\max}$, where $\Delta p(t)$ is the pressure drop caused by the hydrogen absorption at time t, and $\Delta p_{\max}$ is the maximum pressure drop after equilibrium conditions were achieved. Figure 3 shows $\alpha(t)$ curves for some of the samples investigated. The time dependence of $\alpha(t)$ may be expressed in a simple general form utilizing the remaining (unreacted) metal volume $V(t)$ at time t and the initial metal volume V_0 (see, for example, ref. 2):

$$\alpha(t) = 1 - V(t)/V_0 \tag{1}$$

Obviously, various assumptions about the hydride growth in the metal matrix will lead to different time dependences of $V(t)$, and therefore of $\alpha(t)$ [2]. The degree of agreement between such model-derived $\alpha(t)$ curves and the corresponding experimental data is a criterion for the correctness of the assumed models. In addition, visual and metallographic examinations of partly hydrogenated samples were employed in an attempt to determine the method of hydride propagation through the reacting metal. Such a determination may supply further confidence in the specific analysis of the experimental data. Visual examinations of partly (20%–40%) hydrogenated intermetallics revealed partly powdered peeled-off samples. The remaining solid metal pieces were identical in form to the originally introduced pieces but had reduced dimensions. Their weight corresponded exactly to the remaining fraction of unreacted material as determined from the appropriate hydrogen absorption curves. Metallographic pictures did not show any evidence for the presence of additional (hydride) phase in the partly hydrogenated samples. Both the visual and the metallographic examinations indicated fewer cracks and grooves on the partly hydrogenated samples than on the original non-hydrogenated specimen. These observations suggest an advancing interface front (a contracting envelope morphology) for the massive stage of the hydride formation in the intermetallic compound. The samples broke into several pieces, *i.e.*

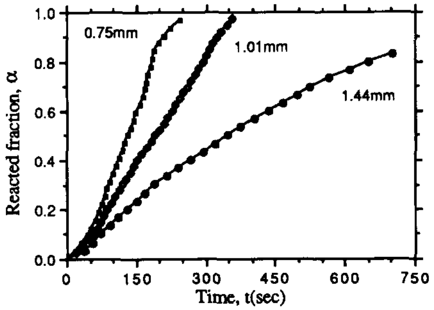


Fig. 3. Time-dependent hydrogen absorption curves at 238 K for several $Zr(Al_{0.2}Fe_{0.8})_2$ samples of different thicknesses as indicated in the figure. $\alpha(t)$ is the reacted metal fraction at time t.

lost their geometrical form, in attempts to obtain higher partial hydrogenations. We did not investigate the exact percentage of partial hydrogenation causing the breakage to occur. It was probably different for the different samples depending on their size, thickness, grooves etc. Assuming a constant hydride propagation velocity of the interface front for a parallelepiped sample yields an unreacted $V(\tau)$ volume:

$$V(\tau) = (b - 2u\tau)(c - 2u\tau)(d - 2u\tau) \tag{2}$$

The dimensions of the parallelepiped are b, c and d, d denoting the thickness. $u(p, T)$ is the interface velocity of the advancing hydride at pressure p and temperature T. τ equals t-t_0. The physical significance of t_0 is the time at which the massive hydrogenation process commences. Obviously eqn. (2) holds only for $u\tau < b, c, d$. The reacted sample fraction $\alpha(\tau)$ is readily obtained by substituting eqn. (2) and $V_0 = abc$ into eqn. (1):

$$\alpha(\tau) = 2u\tau(1/b + 1/c + 1/d) - 4(u\tau)^2(1/bc + 1/cd + 1/bd) + 8(u\tau)^3/bcd \tag{3}$$

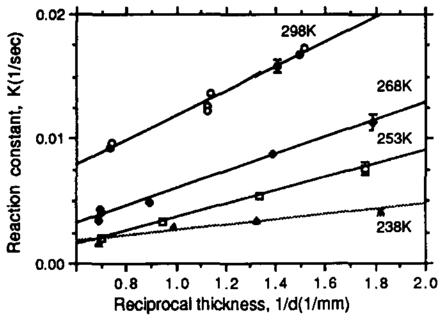
$\alpha(\tau)$ may be approximated by $2u\tau(1/b + 1/c + 1/d)$ for small values of $u\tau$ as compared with the parallelepiped dimensions; the terms containing higher degrees of $u\tau$ in eqn. (3) may then be neglected. In addition, if the thickness d of the sample is significantly smaller than the other parallelepiped dimensions, $1/b$ and $1/c$ may be also neglected. $\alpha(\tau)$ is then approximated by

$$\alpha(\tau) \approx K(p, T)\tau \tag{4}$$

$K(p, T)$ is a temperature- and pressure-dependent hydrogenation reaction constant:

$$K(p, T) = 2u(p, T)/d \tag{5}$$

Equation (4) has the advantage of being identical for all thin samples regardless of their planar shape. The estimated length or width of a typical specimen was about five times larger than its thickness. Usually the $\alpha(t)$ curves exhibited a linear behaviour for 10%–50% hydrogenation, *i.e.* for α values between 0.1 and 0.5. The reaction constants K were determined from the slopes of the linear regions of the $\alpha(t)$ curves. At least four different $\alpha(t)$ curves, each one at a different sample thickness, were measured for each temperature. The interface hydriding velocity $u(p, T)$ was determined from the slope of a line of K plotted as a function of $1/d$: see eqn. (5). Each such line was fitted by utilizing at least four points. Four lines of this type were obtained for the four different temperatures employed in the present work (Fig. 4). In this way four different front velocities $u(p, T)$ were determined, namely at 238 K, 253 K, 268 K and 298 K. An Arrhenius-type behaviour is demonstrated in the plot of ln u *vs.* $1/T$ (Fig. 5), from which an activation energy $E_a = 0.13 + 0.03$ eV was derived for the hydrogenation kinetic process. The linear regression coefficients of the least-squares fits were better than 0.9 in all the cases. In fact we assigned errors σ to each point based on the initial experimental inaccuracies and dispersions. We therefore estimated in each stage of the data analysis the deviations of the derived values by employing a weight $1/\sigma^2$ for each point, *i.e.* utilizing the χ^2 merit function:



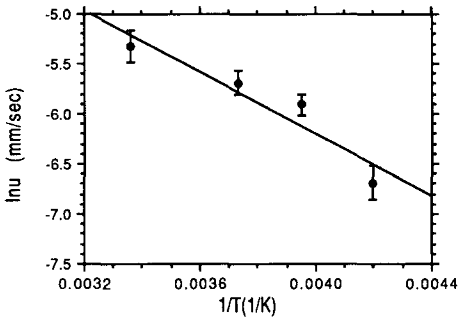


Fig. 4. Plots of the hydrogenation reaction constants K *vs.* the reciprocal sample thickness $1/d$ at four different temperatures as indicated in the figure. The slopes of the fitted straight lines yield the interface velocities $u(T)$.

Fig. 5. A semilogarithmic plot of the interface velocity u *vs.* the reciprocal temperature $1/T$. The slope of the fitted straight line yields the activation energy E_a.

see for example ref. 4 and the computer programming therein. A reasonable goodness of fit was obtained in all cases. More details concerning the error estimations will be published elsewhere.

An additional calculation procedure was also utilized. The coefficients of $(u\tau)^n$, $n=1$, 2, 3, in eqn. (3) were determined for each specific sample from the measured thickness d and the estimated rectangular basis dimensions b and c. Then eqn. (3) was solved for predetermined values of α between 0 and 1, thus obtaining the corresponding $u\tau$ values. The experimental $\alpha(t)$ curves were used to extract the t values corresponding to the measured α values, numerically equal to the previously predetermined 0–1 values. In this way a linear correspondence between $u\tau$ and t was established, and u and t_0 could be determined from the slope and the interception respectively of $u\tau$ *vs.* t. In principle, a good linear regression should exist between $u\tau$ and t over the 0.1–1 range of α. Practically, this occurred usually between 0.1 and 0.7, although in some cases the upper limit extended up to values near 1. In this way at least four u values were determined at each temperature, while one hydride propagation velocity was derived according to the previously described procedure. Mean interface velocities $u(T)$ were calculated for each temperature by averaging all the u values obtained at a specific T. The calculated activation energy E_a according to this procedure, which will be described in more detail elsewhere, is 0.14 ± 0.02 eV (Fig. 6).

Table 1 summarizes the results obtained in the present work.

4. Summary and conclusions

This investigation presents, to the best of our knowledge, the first kinetic results of the massive hydrogenation stage in intermetallic samples of well-

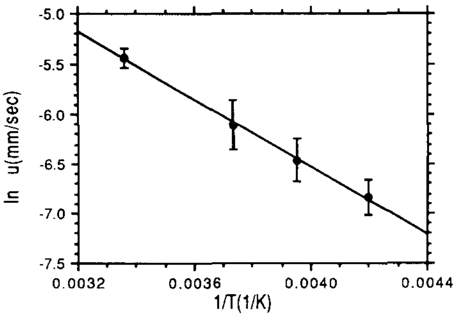


Fig. 6. A semilogarithmic plot of the interface velocity u derived from polynomial fits of $\alpha(t)$ (see text) *vs.* the reciprocal temperature $1/T$. The slope of the fitted straight line yields the activation energy E_a.

TABLE 1

Summary of results

Sample	Thickness (mm)	Temperature (K)	Reaction constant K (10^{-3} s^{-1}) (± 10%–15%)	Hydride interface velocity[a] ($\mu m\ s^{-1}$)	Activation energy[a] (eV $atom^{-1}$)
1	0.71	298	15.9		
2	0.66		17.2		
3	0.89		12.6		
4	0.67		16.8		
5	0.89		12.3		
6	0.88		13.7		
7	1.36		9.2	4.9 ± 0.5	
8	1.35		9.7	(4.4 ± 0.4)	
9	1.43	268	3.8		
10	1.42		4.2		
11	1.12		4.4		
12	0.72		9.7		
13	1.45		3.3	3.4 ± 0.3	
14	0.56		11.5	(2.2 ± 0.6)	
15	0.57	253	7.7		
16	1.42		2.1		
17	1.06		3.4	2.7 ± 0.2	
18	0.75		5.5	(1.6 ± 0.3)	
19	0.76	238	3.5		
20	1.01		2.9		
21	0.55		4.1	1.2 ± 0.1	0.13 ± 0.03
22	1.45		1.7	(1.1 ± 0.2)	(0.14 ± 0.02)

[a] The values in parentheses are those derived from the polynomial analysis (see text).

defined thickness and approximately defined geometrical (parallelepiped) shape. Many papers, which are not reviewed here, have been published on the hydriding kinetics of powdered intermetallic compounds since the first kinetic study of $SmCo_5$ [5]. The only experiment employing a massive intermetallic was performed in the hydrogen solubility region of approximately spherical $LaNi_5$ samples [6]. The use of relatively large $Zr(Al_{0.2}Fe_{0.8})_2$ pieces for the kinetic hydrogenation study significantly reduces the problem of self-heating as demonstrated by measuring the temperature at the reaction chamber. This observation is consistent with the requirement for a minimal sample thickness [7] in the range 0.1–1 mm in order to avoid self-heating during the hydrogenation of titanium. An even smaller heat sink is probably required in the present case as the heat of hydride formation of $Zr(Al_{0.2}Fe_{0.8})_2$ is less negative than the corresponding value for titanium. The second advantage in using pieces of definite thickness and approximately defined geometrical shape concerns the analysis of the experimental data as well as the possibility of inspecting visually some of the assumptions employed in this analysis.

The main conclusion of the present work is that the hydride formation in the $Zr(Al_{0.2}Fe_{0.8})_2$ intermetallic proceeds through a constant velocity movement of the hydride–metal boundary (contracting envelope). The so-called intrinsic kinetic parameter [2] is determined to be the interface velocity u. The derived values of u indicate high hydriding velocities as compared with some simple metals such as titanium, uranium, gadolinium and hafnium [7–10]. Both methods of analysis employed in the present work have some limitations, *i.e.* have been carried out under certain approximations. The linear expression (4) neglects higher terms of eqn. (3). On the contrary, utilization of eqn. (3) for deriving the interface hydriding velocity u assumes an approximately parallelepipedal shape, while only the sample thickness is strictly defined. These approximations and the sample breakage above certain hydrogenation levels limited the range of fitted α values. The latter analysis procedure yields, as expected, somewhat lower u values (Table 1 and eqns. (2)–(4). Either way, the activation energy E_a derived from Fig. 6 is only slightly higher than that obtained from Fig. 5.

The rate-limiting step of the hydrogenation process in $Zr(Al_{0.2}Fe_{0.8})_2$ has not been determined in the present work. The conclusion of a constant velocity contracting envelope hydride propagation limits, however, the possibilities to three [2], namely a hydride–metal interface controlled process, or diffusion through a protective non-adherent hydride film of an apparently constant thickness, or surface processes occurring on a non-adherent hydride film with an apparently constant thickness.

Kinetic measurements of additional intermetallic compounds of the $Zr(Al_xFe_{1-x})_2$ system are under way in order to shed some light on the anomalous inhibition of hydrogen absorption in this system for large x values. We hope to perform also some pressure-dependent measurements of the interface velocity u in an attempt to determine the rate-limiting step for the hydrogenation process in these intermetallic compounds.

Acknowledgments

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