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A reaction–diffusion analysis of the hydriding kinetics of zirconium-based alloys

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Abstract

One of the most critical points when studying hydriding kinetics of intermetallic compounds is to determine internal kinetic parameters (IKP) independent of sample geometry that allow to compare different systems. In this sense, theoretical modelling of the microscopic mechanisms taking place during the reaction is fundamental. In this work, we present a reaction–diffusion model for the hydrogen absorption in bulk Zry-4 samples. The model is based on two IKPs, easily measurable by simple experimental techniques: the hydrogen diffusion coefficient in the matrix and the reaction rate. Different relationships that arise from the model between measurable quantities (e.g. the hydride front velocity) and the IKPs are presented. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Considerable work has recently been done to understand the microscopic mechanisms that control the hydriding kinetics in metals and intermetallic compounds. A great variety of behaviours can be observed in the systems of interest due to the fact that different processes control the absorption kinetics. While the experimental data show that surface-related processes (surface diffusion, chemisorption) are usually the slowest stages during hydrogen (H) absorption [1], vacuum-annealed Zr-based alloy samples [2–4] have shown a kinetic limited by the hydriding reaction itself, leading to a kinetic of contracting-envelope type. In all these cases, the main problem is not only to identify the different processes contributing to the overall reaction but to determine an internal kinetic parameter (IKP) independent of sample geometry to compare different systems. In order to get an adequate IKP, several approaches have been made. The most common assumption is to analyse the overall absorption reaction as a consequence of several microscopic steps that occur sequentially with one of them considerably slower than the rest. Several systems match this assumption and recently some reaction models for the composition and decomposition of metal hydrides with one rate-determining partial reaction step have been presented [5,6]. However, this approach to the problem of getting an IKP is not suitable when there are more than one steps occurring simultaneously. A possible approach for dealing with this kind of situation is to elaborate a model based on all the necessary physical assumptions and numerically solve it. Even though this approach can be more complicated, values of IKPs obtained by these methods tend to be more realistic.

With the aim of finding a suitable set of IKPs for the case of H absorption kinetics in Zry-4 we have developed a reaction-diffusion model based on a set of realistic physical assumptions for this system. Most intermetallic compounds, and in particular Zry-4, are characterised by the cracking of the reacting sample during the activation process. The mechanism of crack formation in Zry-4 is such that thin flakes of tenth of micrometers are formed and eventually fall off the sample. The problem of taking into account this process to analyse H absorption in massive samples had not been faced until Bloch [7] presented a model that

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introduced two IKPs, the velocity at which the microlayers form and leave the sample (the peel-off velocity U_p) and the velocity at which hydriding occurs in these layers (U_h). He assumes that reaction kinetics in the microlayers follows a contracting-envelope law and that both, U_h and U_p are constant.

Here we face the problem from another point of view. We try to explain the observed H absorption kinetics by modelling the diffusion of H through the bulk and the reaction of H with the metal matrix with reaction–diffusion type equations. This approach appears more 'fundamental' than the previous model, despite its obvious complication. The model used previously reported assumptions but introduced the mechanism of peeling-off in a simple way. The results of the computer simulation allowed us to find several relations between easily measurable quantities and the proposed IKPs. The model reproduces well most of the observed behaviours in a wide temperature and sample size range facilitating the analysis and understanding of experimental data.

2. The reaction–diffusion approach

As the presented model was developed for analysing Zry-4 experimental data, specific hypotheses have been made. Possible extensions of this model to other systems are restricted to fully satisfy all these assumptions.

We will ask the model to reproduce the experimental observation of H absorption in parallelepiped-geometric samples of size $a \times a \times b$ where H is picked up only by one of the $a \times a$ faces [8]. With the resulting model we will solve a unidimensional case but it can be easily extended to any more-general case.

The pick-up of H starts from the $a \times a$ treated surface with concentration gradient as the driving-force for getting into the sample [8]. After the reaction begins, several portions of the sample transform from the initial α-phase to the hydride δ-phase. Previously reported data confirm that H diffusion through the hydride phase is much smaller than through the α-phase [9], thus, another assumption comes from the fact that H flux through any transverse surface can be considered as proportional to the fraction of area available for the α-phase (A_α). We will consider that this fraction is numerically equal to the volumetric fraction of α-phase in that point (v_α). Thus, we will have an effective diffusion coefficient equal to the actual D_α but multiplied by the available fraction of surface (A_α/A_α), considered here as numerically equal to v_α. The effective diffusion coefficient will thus be $D = D_\alpha v_\alpha$.

The model of the reaction term we use here is the expression for the reaction term proposed by Marino et al. [10]. It considers that reaction starts when local H concentration in α-phase overcomes the terminal solid solubility (TSS) at that temperature while the global concentration varies low enough to assure that δ- and α-phases are nearly the local equilibrium so the chain-rule can be applied. This term introduces a parameter p, related with the rate of hydride precipitation. The reaction term also includes a morphology factor considered here as $v_\alpha^{2/3}$, from the consideration of spherical nucleation centres for δ-phase growth. Small variations around the 2/3 value have a negligible influence on the numerical results, so its effect will not be analysed here.

As mentioned, the main contribution of this paper is the treatment of the peeling-off process. The formation of microlayers during H absorption is directly related with the difference in specific volume between α- and δ-phases. When δ-phase grows it generates stress in the metal matrix only relaxed by crack formation. Clearly, while at low H concentration there are no cracks, the sample is completely peeled-off when the δ-phase is fully developed. We assume here that the peeling-off process occurs when the volumetric fraction of δ-phase reaches a critical value v_{cr}. In this model, this is considered as follows (see Fig. 1):

- H reaches any point of the sample after diffusing through the α-phase from the sample surface.
- The previous process goes on up to a H concentration equal to TSS when the δ-phase appears. The H that comes from the surface can contribute there in two different ways: feeding the reaction in the point or diffusing towards the rest of the sample.
- When the volume fraction of δ-phase reaches a critical value v_{cr}, the sample cracks and thus H can be taken in this point directly from the pressure reservoir without diffusing from the original surface. Thus, the peeled-off part of the sample follows with its reaction in a faster way.

It is important to remark that values of v_{cr} are of great interest in structural applications because they

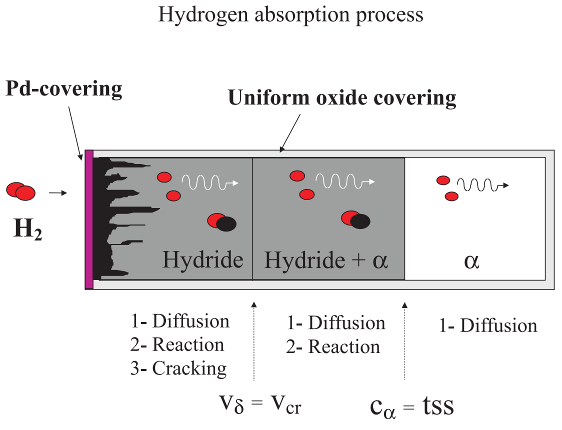

Fig. 1. Proposed regions in the sample during H absorption.

determine the volumetric fraction of hydride phase necessary for crack development. In addition, this value can be compared with those obtained from measurements of mechanical properties or crack growth.

Thus, two main variables have to be modelled: the H concentration in the α-phase (C_α) in H atoms per Zr atom (H/Zr ratio) and the volumetric fraction of α-phase (v_α). The volumetric fraction of δ-phase (v_δ) clearly obeys $v_\alpha + v_\delta = 1$. For simplicity, H concentration in the final hydride phase C_δ can be considered constant. Based on all the previous arguments the equations that govern the absorption process are

$$\partial_t c_\alpha = D_\alpha \partial_x^2 c_\alpha + \frac{D_\alpha}{v_\infty} \partial_x v_\alpha \partial_x c_\alpha - p(c_\alpha - \mathrm{TSS})(c_\alpha - \mathrm{TSS}) v_\alpha^{-1/3} \tag{1}$$

and

$$\partial_t v_\alpha = -p\theta(c_\alpha - \mathrm{TSS}) \frac{(c_\alpha - \mathrm{TSS})}{(c_\alpha - c_\alpha)} v_\alpha^{2/3}, \tag{2}$$

where the $\theta(y)$ function is zero for $y < 0$ and 1 for $y > 0$ ($y = C_\alpha - \mathrm{TSS}$). For all the calculations we have taken values of TSS and C_δ from the equilibrium phase diagram for the Zr–H without considering any effect of hysteresis in the absorption reaction. Regions where $v_\alpha = 0$ are considered in equilibrium with the pressure reservoir i.e., H concentration is considered fixed to C_δ value. In the regions where $v_\alpha = 1$ we solve the usual diffusion equation for C_α. The moving interfaces $\delta/\alpha + \delta$ and $\alpha + \delta/\alpha$ are treated considering the Rankine–Hugoniot condition that relates the concentration jump across the interface with the interface velocity assuming hydrogen conservation. The condition states that at the interface $j.\vec{n} = C(\vec{v}.\vec{n})$ with C the concentration jump. Thus, the IKPs suggested in this model are the H diffusion coefficient through the α-phase and the rate of reaction p and both can be measured by other techniques (e.g., permeation). Clearly both are independent of sample geometry, although the model and the results presented here are for the unidimensional case.

3. Results

We solved Eqs. (1) and (2) using different conditions (temperature, sample size) to find out qualitative relationships between IKPs and measurable quantities. As it was mentioned before, the reaction of Zr-alloys with gaseous H starts with H diffusion through the initial α-phase followed by the formation of different hydride phases. The H absorption kinetics is usually shown by plotting the equivalent fraction of the reacted sample $\xi(t)$ against time. Clearly, $\xi(t)$ varies from 0 to 1. The use of a surface treatment developed in our laboratory [8] facilitates the growth of a uniform hydride front from only one face towards the rest of the material. A first achievement of the model is that the free interplay between the different mechanisms mentioned above leads to the formation of a reaction front that moves at constant velocity. Thus, the formation of this front and the invariance of its velocity are derived properties of this model, not a priori hypothesis. It has already been observed that the front advancing at constant speed can only be observed above a critical value L_{cr} of the sample length [8]. From the observation of different numerical resolutions of the model, we can determine the geometrical condition for the existence at a given temperature of a time interval at which front velocity is constant. This condition can be well approximated by

$$L > L_{\mathrm{cr}} \approx \sqrt{\frac{v_{\mathrm{cr}} D_\alpha}{p}} \tag{3}$$

with v_{cr} the value of the critical volume fraction of δ at which crack formation occurs. Fig. 2(a) shows a set of

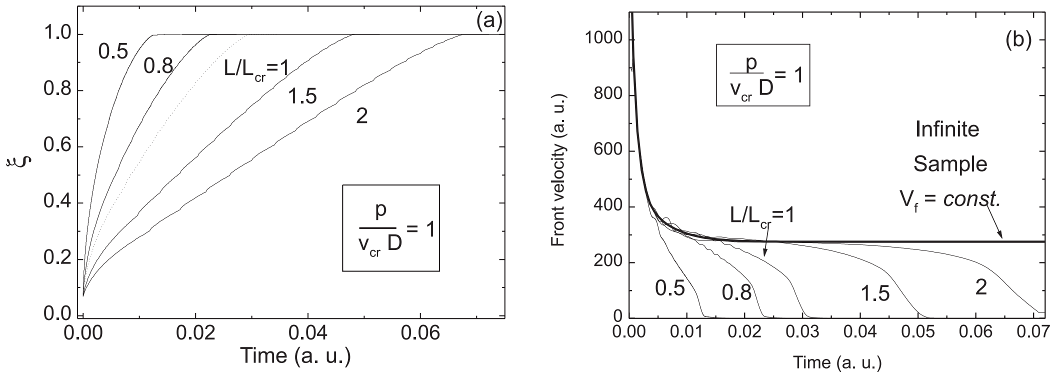

Fig. 2. (a) Calculated absorption curves for different sample lengths and $L_{\mathrm{cr}} = 1$, (b) the corresponding front velocity. Note the constant value of v_{f} for $L > L_{\mathrm{cr}}$.

absorption curves for the case $p/v_{cr}D_\alpha = 1$, i.e., $L_{cr} \sim 1$. The different curves correspond to different sample lengths. As can be seen, the last of the linear stage in the absorption curves is a function of L/L_{cr}. Fig. 2(b) shows the front velocity $v_f = L d\xi/dt$ for the same set of parameters. It can be seen that samples with $L/L_{cr} > 1$ have a range of constant velocity as expected in an infinite sample while for L/L_{cr} there is no constant velocity at any time.

As mentioned, another important point in the comparison with experimental data is the determination of the front velocity v_f as a function of p and D_α, once the condition (3) is satisfied. Fig. 3 shows a plot of $v_{cr} v_f^2/D_\alpha$ as a function of p. As can be seen, for several v_{cr} values the data follow a linear law that allows to express the front velocity as

$$v_f^2 \approxeq 600 \frac{pD_\alpha}{v_{cr}}. \tag{4}$$

Eqs. (3) and (4) can be combined to eliminate p obtaining

$$v_f \approxeq 25 \frac{D_\alpha}{L_{cr}} \tag{5}$$

an equation that relates three measurable quantities, D_α, v_f and L_{cr}. This equation is not only a very useful relation when measuring hydriding kinetics but an easy way to test the proposed model. On the other hand, experimental data can be analysed in terms of Eq. (5) looking for deviations from the constant value predicted for the $v_f L_{cr}/D_\alpha$ ratio. Such deviations can be thought to be directly related to deviations from the set of hypotheses listed above.

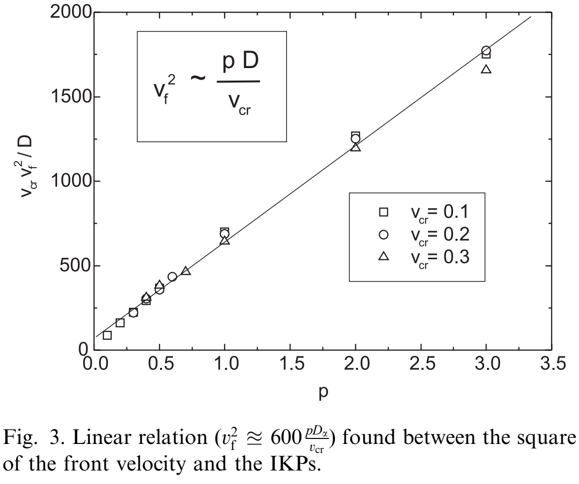

Fig. 3. Linear relation ($v_f^2 \approxeq 600 \frac{pD_\alpha}{v_{cr}}$) found between the square of the front velocity and the IKPs.

4. Comparison with experimental data

Measurements of hydriding kinetics in Pd-covered Zry-4 samples of $4 \times 4 \times 27.5$ mm^3 were performed at constant temperature and pressure in a closed chamber following the technique described in [11] (see Fig. 4). As mentioned above and according to Eq. (3) a hydride front develops and moves along the samples as confirmed by SEM analysis of partially hydrided samples, (see Fig. 5). Values of the front velocity for several temperatures are listed in Table 1. Fig. 6 shows an Arrhenius plot of the front velocity which confirms that its development is a thermally activated process, as expected considering Eq. (4) and that diffusion and reaction are thermally activated processes too. The value of 54 KJ/mol found for the activation energy is close to previously reported values for vacuum-annealed Zr samples [2]. Measurements of hydriding kinetics of

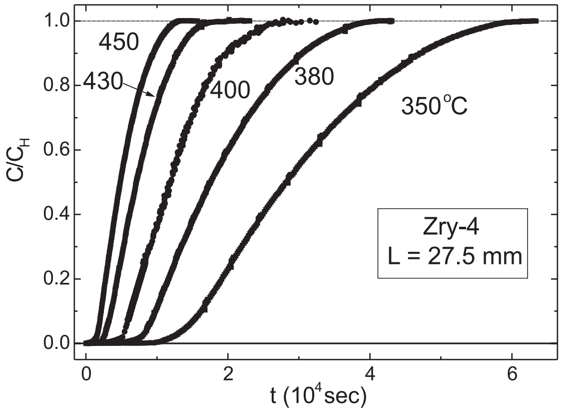

Fig. 4. H absorption kinetics for Zry-4 samples in the temperature range 350–450°C. Sample length = 27.5 mm. C_H = 21 500 ppm by wt.

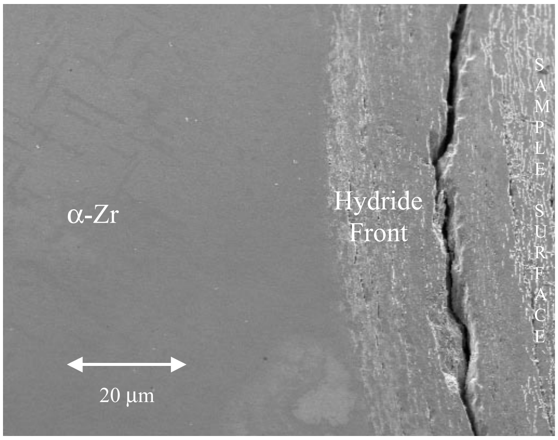

Fig. 5. SEM micropraphy of a partially hydrided Zry 4 sample. The development of a hydride front can be seen.

Table 1
Experimental data for the front velocity and the critical length of Zry-4 for several temperatures[a]

Temperature (K)	v_f (μm/min)	L_{cr} (mm)	D_α (10^{-4} mm^2/s)	$V_f L_{cr}/D_\alpha$	p^{-1} (min)
623	60	$< 3 \pm 1$	1.24	24 ± 8	68
653	80	–	1.86	–	45
653	125	2 ± 1	2.38	17 ± 9	19
703	190	–	3.37	–	19
723	245	–	4.81	–	15

[a] The diffusion data were taken from [11]. Values of p were obtained by choosing $v_{cr} \sim 1\%$.

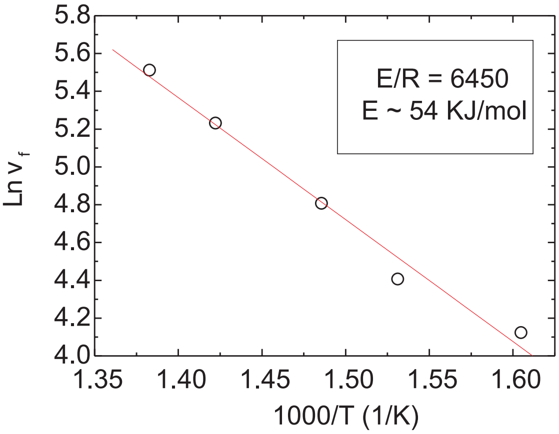

Fig. 6. Arrhenius plot of the measured front velocity in Zry-4. The found activation energy is $\Delta E = 54$ KJ/mol.

samples of $4 \times 4 \times L$ mm^3 with L ranging from 1 to 5 mm allow us to estimate the critical length at two different temperatures finding $L_{cr} \sim 3$ mm and roughly independent of temperature within the scatter in the range 300–450°C. With previously reported values of the activation energy for H diffusion in the Zr matrix of $\Delta E = 44$ kJ/mol [11], and considering our results on the temperature dependence of v_f, we have that the activation energy for the reaction is of about $\Delta E_p = 64$ kJ/mol. Expression (5) suggests that the critical length should decrease with increasing temperature. The expected variation for the critical length between 300°C and 450°C should be about 1 mm, which is a value not clearly distinguishable in our experimental data though preliminary results seem to confirm it. Table 1 also presents the calculated values for $v_f L_{cr}/D_\alpha$. Although there is no experimental information available to test relation (5) the two measured points follow well the proposed relation.

Finally, we obtained from our data and through the model values of p to compare with those obtained by Marino et al. [10] from measurements on supercharged samples. The obtained values (see last column in Table 1) are consistent with those presented in [10] if the critical volume fraction value is chosen as 1%. Remembering that v_{cr} is the fraction of δ-phase at which cracks appear, the value of 1% seems to be quite small, though the lack of previous results that could help to compare with avoids the possibility of a more precise analysis. The oversimplified way in which we considered crack development dynamics should be studied in detail, particularly considering the influence of microstructure and how internal stresses and hydride-forming precipitates facilitate cracking.

5. Conclusions

In the analysis we presented a model to analyse H absorption in Zr-alloys. H diffusion in the bulk and the rate of reaction are the internal kinetic parameters that simplify the analysis of the global problem. From simulations of the process a phenomenological expression was obtained relating the hydride front velocity, the diffusion coefficient and the critical length for observation of stationary stage during front advance. In order to test these expressions, measurements of the critical length and front velocity can be obtained from H absorption kinetics measurements using standard Sieverts technique while the effective diffusion coefficient can be measured by permeation techniques. The rate of reaction p can be obtained by measuring the precipitation times of an oversaturated specimen [10]. Expression (4) provides a rough estimation of the critical volume fraction of δ-phase needed to initiate the peel-off process. The influence of internal stresses and second phase precipitates in the cracking process should be considered to evaluate the cracking susceptibility of the alloy. We suggest to perform similar measurements on stress-relieved samples and/or pure zirconium to analyse separately both effects on the critical volume value. Although the experimental observations and the analysis presented here are one-dimensional, extension to more general cases follows straightforward.

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