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Analysis of the hydride formation kinetics of Zry-4

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Abstract

One of the most critical points when studying the hydriding reaction of Zr-based alloys is to determine internal kinetics parameters (IKP) independent of sample geometry that allow to compare hydrogen embrittlement of different compounds or the same alloy with different properties, e.g. constituents, microstructure or texture. In this sense, the design of new experiments and the theoretical modelling of the microscopic mechanisms occurring during hydrogen absorption are fundamental. In this work, we study the hydrogen absorption kinetics during activation of Zry-4 massive samples of standard and modified composition. During the reaction and due to the difference in specific volume between Zr and its hydride, the sample disintegrates by consecutive peelings of thin microlayers of approximately 20 μm of partially reacted material. This peeling process, coupled with the hydride reaction, leads to a linear stage in the overall absorption kinetics related to a hydride front of δ-phase that develops and grows at constant velocity from the sample surface. The hydride front velocity was measured for different sample geometry in the temperature range from 200 to 400°C. The activation energy associated with the process of advancing front was 54 KJ/mol. The value of this velocity at a given temperature as well as the activation energy can be used as an appropriate IKP for simulation or comparisons among different Zr-based alloys. We also evaluate the changes in activation energy and hydride front velocity due to modifications in microstructure and for different compositions of the microalloying materials (Ni, Fe and Cr). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zry-4; Hydriding kinetics; Hydrogen embrittlement

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1. Introduction

A 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 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 kinetics limited by the hydriding reaction itself, leading to kinetics 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 also to determine an internal kinetics parameter (IKP) independent of sample geometry to compare different systems. Several approaches have been made to get an adequate set of IKPs. The most common assumption is to analyse the overall absorption reaction as a consequence of several microscopic steps that occur sequentially with one of these steps 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 [5–7].

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 [8]. Most of intermetallic compounds, and in particular Zry-4, are characterised by cracking of the reacting sample during the activation process. The mechanism of crack formation in Zry-4 is such that thin flakes of several micrometers (~20 μm) are formed and eventually fall off the sample. The problem of taking into account this process in the modelling of H absorption in massive samples had not been faced until Bloch [9] presented a model that introduces 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 present experimental results on the hydriding kinetics of Zry-4 obtained under different temperatures and

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in samples of diverse geometry. As a result of our experimental set-up, we are able to get a homogeneous hydride front of δ-phase moving at constant velocity through the entire sample. Values of the hydride front velocity are also presented as well as values of its activation energy. Preliminary results on the effect of sample microstructure suggest that the front velocity decreases with increasing grain-size without affecting the activation energy. In addition, preliminary results on the effects of microalloying elements show that the activation energy for the overall absorption process is markedly affected by the increase of Fe, Ni and Cr content, suggesting that they are involved in the mechanisms that contribute to the absorption process. All the data are interpreted using the presented reaction–diffusion model [8].

2. Experimental details

The equipment used to measure hydrogen absorption kinetics at constant pressure is shown in Fig. 1. It consists of a fixed volume that has a pressure gauge and is immersed in a bath at fixed temperature. The volume is connected to a hydrogen reservoir through a flux controller. The absorption kinetics is measured by computing the changes in pressure monitored by a pressure sensor. When the change in pressure is higher than 1% of the selected value a flux controller compensates this change. A PC-based data acquisition system monitors and controls pressure, temperature and hydrogen flux. Hydrogen absorption kinetics measurements were obtained at a hydrogen pressure of 30 bar and temperatures ranging from 350 to 450°C.

The samples were rectangular parallelepipeds of dimensions $4\times4\times L$ mm ($L=\sim27.5$ mm). The starting material was taken from a pilot plant size ingot of Zry-4 alloy of standard nuclear grade composition (ASTM B 350). From this alloy, samples of standard and intentionally modified composition were prepared by arc melting plus suitable thermomechanical treatments. The samples with modified compositions were obtained by re-melting the standard alloy with suitable amounts of the microalloying elements to obtain an increase of 0.025, 0.1, and 0.09 wt% in Ni, Fe and Cr, respectively. All alloy samples were buttons of about 40 g which were hot rolled at 700–800°C undergoing a reduction in thickness of about 50% after three lamination runs. In this way the solidification microstructure was smoothed out and the typical α-phase platelets observed by SEM showed practically no preferred orientation. Then samples were cut to final dimensions by using either a diamond wafering blade or a jeweller saw. Finally a stress relief annealing at 450°C for 2 h was given to the samples encapsulated in quartz under argon.

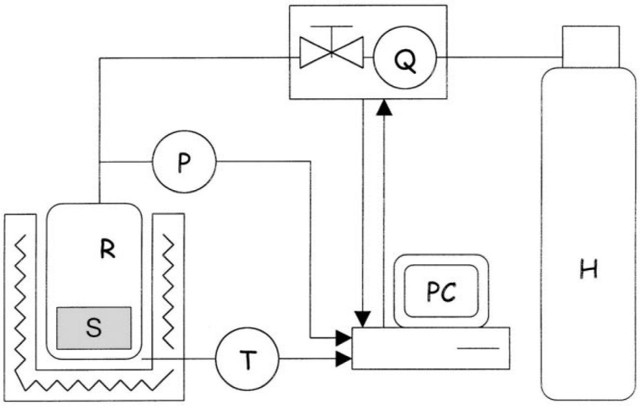

Fig. 1. Experimental set-up used to measure hydrogen uptake. P,T: pressure and temperature gauges; Q: flowmeter of the flux controller; H: hydrogen reservoir; R: fixed volume reactor chamber; PC: personal computer with data acquisition system and S: Zry-4 sample.

The hydride phase development was studied by metallographic examination of the cross-sections of partially hydrided samples. Samples were chemically cleaned with a solution of lactic, nitric and hydrofluoric acids in volume ratios of 50:45:5, respectively, and immediately placed into the vacuum chamber of a sputter coating system. One of the faces of 4×4 mm^2 was etched using argon bombardment and then covered with a Pd film of about 50 nm thick by sputtering under purified Ar atmosphere. Impurities in Ar were: $H_2O<5$ ppm; $O_2<5$ ppm; $N_2<2$ ppm. This experimental technique developed in our laboratory allows H to be absorbed only through the Pd-covered face simplifying the analysis of the results [8].

To increase the grain size, samples were annealed for 30 days at 500°C in Ar atmosphere. The average grain size increment was from 20×100 μm to 30×120 μm. No weight losses, composition modifications or micro-precipitate growth were observed.

3. Results and discussions

Fig. 2 shows a typical curve of the fraction of reacted sample as a function of time. The fraction reacted is understood to be the total number of hydrogen atoms absorbed per metal atom at time t divided by the maximum absorption capacity of the system.

The final concentration is always (2.1±0.1) wt%, which strongly suggests a ZrH_2 stoichiometry. A face centre tetragonal structure with $c/a=0.976$ ($a=0.497$ nm) was obtained for a completely hydrided specimen from the X-ray diffraction pattern. The final hydrogen concentration [10] and the hydride structure and lattice parameters [11] show that ϵ-phase is the equilibrium phase under the experimental absorption conditions.

A thorough analysis of the H uptake data presented in Fig. 2 shows that three different stages can be clearly identified [8]. First, a stage in which concentration starts increasing linearly with time and then speed up. Then, a second stage in which concentration rapidly increases

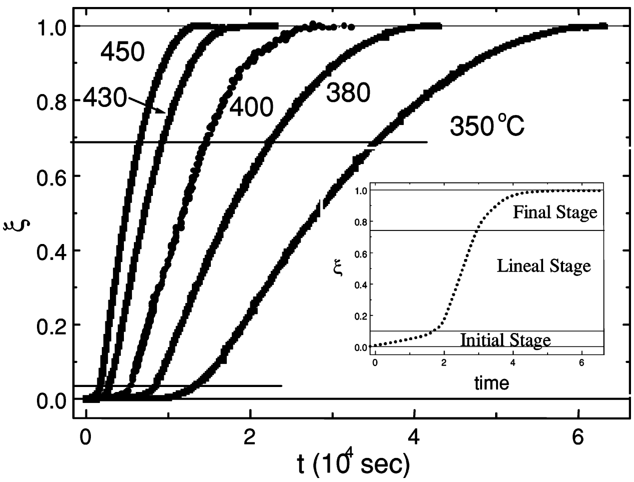

Fig. 2. Hydrogen absorption kinetics measurements for five selected temperatures.

linearly with time. Third, a final stage where all the reactant material is used up and the hydriding reaction stops. The value of the fraction of the reacted sample where a change of stage is produced depends on sample length.

We will only deal here with the second stage. It starts when a small layer of hydride is formed on the sample surface. Neglecting the transition between the first and second stage we found the second stage to evolve linearly with time. Fig. 3 shows a micrograph of a sample at the beginning of the second stage. Here, a hydride front develops and moves along the entire sample. The formation of a hydride front has been observed before [2,12]. The linear dependence with time of the average hydrogen concentration can be explained if we assume that this front is moving along the sample at constant velocity. All the samples studied showed that the hydride front is a layer of about 0.5 mm of thickness. The rest of the hydride material breaks up due to the stress caused by the difference in specific volume between hydride and Zry-4. A model for explaining that the front velocity is a constant was recently published by the authors [8]. The stationary stage can be understood with the aid of Fig. 4 that shows the four different regions coexisting in a sample while the hydride front moves. From the treated face, where H is initially picked up, it can be observed the fully hydrided peeled off material (ϵ-phase), grains of peeled off material where H is still being absorbed ($\epsilon+\delta$-phase), the cracked zone of the sample ($\delta+\alpha$-phase) of width L that moves inside the bulk at a velocity v_f and the non-cracked zone of the sample where hydrogen concentration diminishes in a critical length labelled L_{cr} in the figure. This stationery stage is obtained when the rate of H absorption in the massive region of the sample, the rate of peeled off material and the velocity of fully hydriding (up to ϵ-phase) of peeled off material are constant. In the massive region the rate-controlling step is then the diffusion of hydrogen through a cracked δ-hydride product layer of constant thickness, as has been suggested before [11].

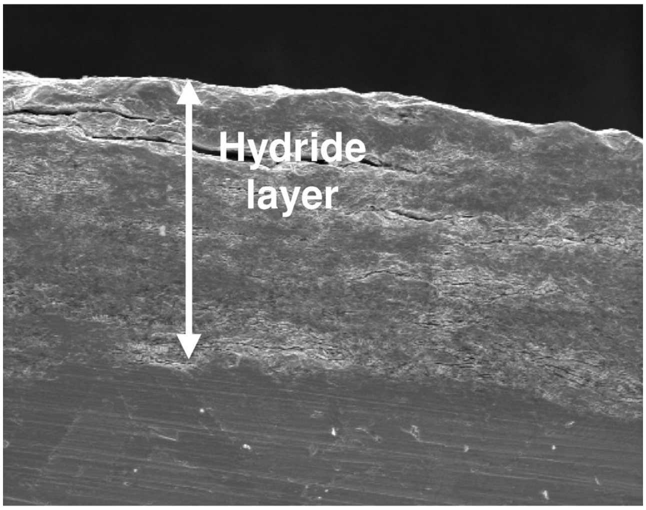

Fig. 3. Cross-section SEM micrograph of a partially hydrided sample with 1 wt% of average hydrogen concentration. The uniform hydride layer is remarked.

From an Arrhenius plot of the hydride front velocity we can obtain an activation energy value of $E=54$ KJ/mol [8] for this process that can be used as a parameter to compare hydrogen uptake in different materials. The available data in the literature [2] is the activation energy for pure Zr. In this case the measurements were made using the usual Sievert's technique, which does not keep the pressure constant. They found an activation energy value of 67 KJ/mol for the hydride front velocity. This higher activation energy value is probably due to the absence of precipitates in the matrix and the morphology of the samples after the thermal treatments they made to them. First, hydriding of second phase precipitates in Zry-4 helps cracking and hydrogen diffusion. Second, Bloch [2] made the measurements after the sample is treated at high temperatures under high vacuum to dissolve the oxide

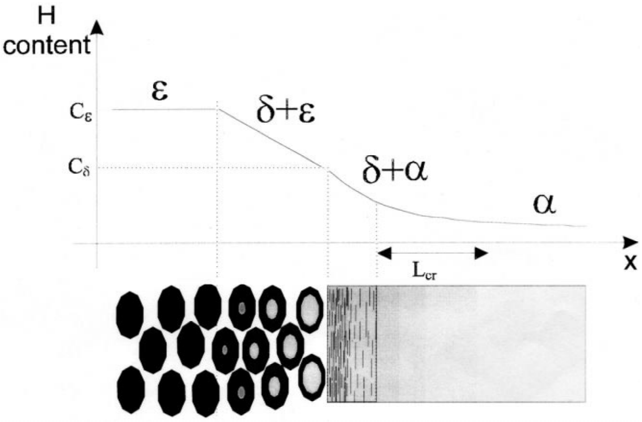

Fig. 4. Schematic diagram showing the different region and H concentration during the second stage.

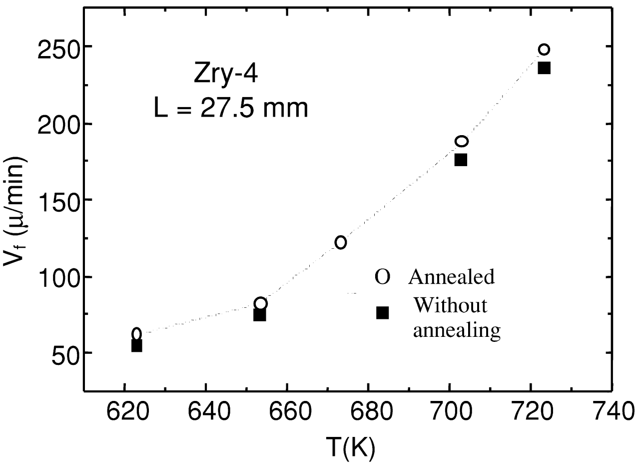

Fig. 5. Front velocity for samples with modified grain size.

layer. This treatment has the disadvantage of producing samples with very big grains. In the present case, the samples were treated with no heating up and thus the grain sizes were considerably smaller. The precipitates, the smaller grain size and the absence of intragranular oxide helps crack formation and thus improves the hydride front velocity.

Grain size effects were studied in samples annealed at 500°C. The results are shown in Fig. 5. As it can be seen, the values of the front velocity are slightly reduced by the increased grain size. Fig. 6 shows the corresponding Arrhenius plots, which suggest the activation energy value is not modified by the grain size. According to [13], this is compatible with a minor grain-boundary contribution to the overall diffusion in α-phase.

The effect of microalloying was also studied by determining the modifications in front velocity and activation energy for samples with different concentrations of the main microalloying elements of Zry-4: Fe, Cr and Ni. Results for the activation energies obtained are shown in Fig. 7.

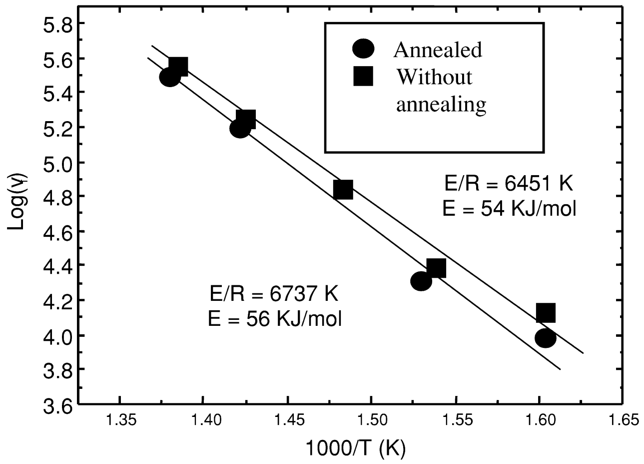

Fig. 6. Arrhenius plot for the front velocity obtained from the kinetic curves of Fig. 5.

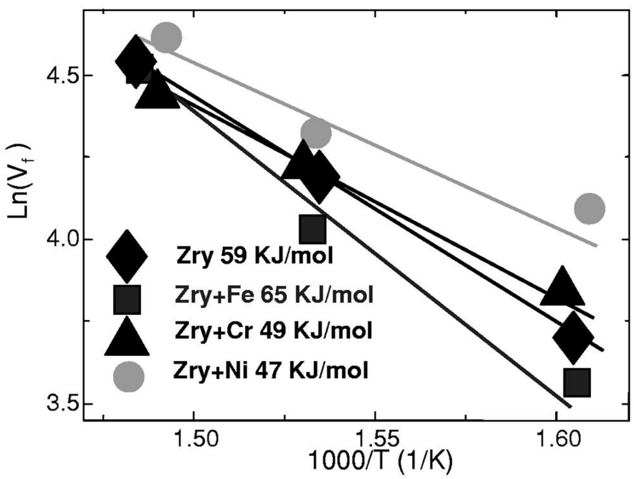

Fig. 7. Activation energies for the front velocity of standard Zry-4 and samples with additions of Fe, Cr and Ni, respectively.

The activation energy changes with variation of microalloying elements. This implies that precipitates are involved in the mechanisms of hydrogen diffusion, hydride precipitation or cracking of the samples. As Fe and Cr precipitate in the form of Laves phases, together with the fact that they are always located in the grain boundaries, it may be expected that its influence is associated with hydrogen pick up and hydriding. The associated increase in volume of these precipitates could be a possible driving-force for the cracking mechanism acting even before the corresponding volume increase associated with zirconium matrix.

4. Conclusions

We have performed hydriding kinetics measurements in Zry-4 samples, analysing the uniform hydride front formation and evolution. The surface treatment performed [8] and the measurements at constant pressure strongly simplify the analysis of the obtained data. We found three different stages for the hydrogen uptake. In the second stage, hydrogen uptake evolves linearly with time that can be attributed to the formation of a hydride layer of constant thickness that moves along the sample with constant velocity of about 100 μm/min at 380°C. The activation energy for the hydride front velocity was found to be 54 KJ/mol, lower than the previously reported value for pure Zr of 67 KJ/mol. The higher value for pure Zr samples can be attributed to the absence of precipitates and the thermal treatments made to the samples. The effect of grain size and microalloying was also evaluated. We found that increasing the grain size diminishes the front velocity without affecting the activation energy. Although the addition of Fe, Cr and Ni markedly modifies the activation energy of the overall absorption process it cannot be precisely identified the main contribution of each one because of their interactions in the formation of second phase precipitates embedded in the Zr matrix.

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