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Deformations induced by high loading ratios in palladium–deuterium compounds

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Abstract

The strong concentration gradients produced during the loading process in palladium hydride are responsible for the well known difficulty in obtaining high loading ratios (H(D)/Pd≈1). Experiments on electrolytic loading of palladium with deuterium have been carried out in which the loading ratio was monitored through a four wire resistance technique. Preliminary results show that dynamic loading strongly affects the maximum ratio achievable.

Keywords: Palladium; Deuterium; Self-stress

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1. Introduction

When hydrogen (and its isotopes) dissolves into metals, it occupies the interstitial positions and expands the lattice. This process generates a corresponding stress field. High concentration gradients in the palladium cause high stress gradients that can inhibit the diffusion process itself. The diffusion flux is described by the general equation:

$$J = -M.c\nabla\mu \tag{1}$$

where c is the hydrogen concentration, M the mobility (related to D, diffusion coefficient by the Einstein relation $D = c\frac{\partial\mu}{\partial c}M$) and μ is the chemical potential. The stress indicated by hydrogen diffusive flux will cause an inhomogeneous distribution of the solute. The Eq. (1) will be in this case:

$$J = -D\left(\nabla c - \frac{c\bar{V}}{RT}\nabla\sigma\right) \tag{2}$$

where $\bar{V}$ is the molar volume of hydrogen in the metal and σ is the stress field. Kandasamy [1] showed that a strain field could stop the diffusion of hydrogen driven by the concentration gradient.

Two approaches can be taken to avoid this inhibition of the diffusion process. Firstly, the concentration gradients (and the adverse stresses) can be minimised during the loading sequence. The second approach is to relieve the stresses generated in the metal through dislocation slipping.

A slow loading procedure minimizes the concentration gradient but, because of the very low ($\approx 10^{-8}$ cm^2 s^{-1}) diffusion coefficient, this solution is not practical as the loading time would be prohibitively longer. Moreover, during the loading, regions of higher lattice parameter, β phase, grow within the α phase regions. In the $\alpha+\beta$ region, the lattice parameter mismatch at the border between the two phases generates a very strong localized stress field which is unfavourable for diffusion [2]. Coexistance of $\alpha+\beta$ phases can be avoided during the loading process by selecting an appropriate path on the p–$c(D)$–T diagram.

Internal stress generated during the loading process can be removed by dislocation slipping, hence the initial metallurgical state of the sample is very important in reducing the blocking force arising from the strain field.

2. Experimental results

Palladium rods (∅ = 0.2×14 mm) were subjected to cathodic discharge in 0.1 M LiOD. The samples (all coming from the same batch), were annealed under vacuum for 0.5 h at 900 °C. After that some of them were gas loaded, following a path that avoided the coexistance of α

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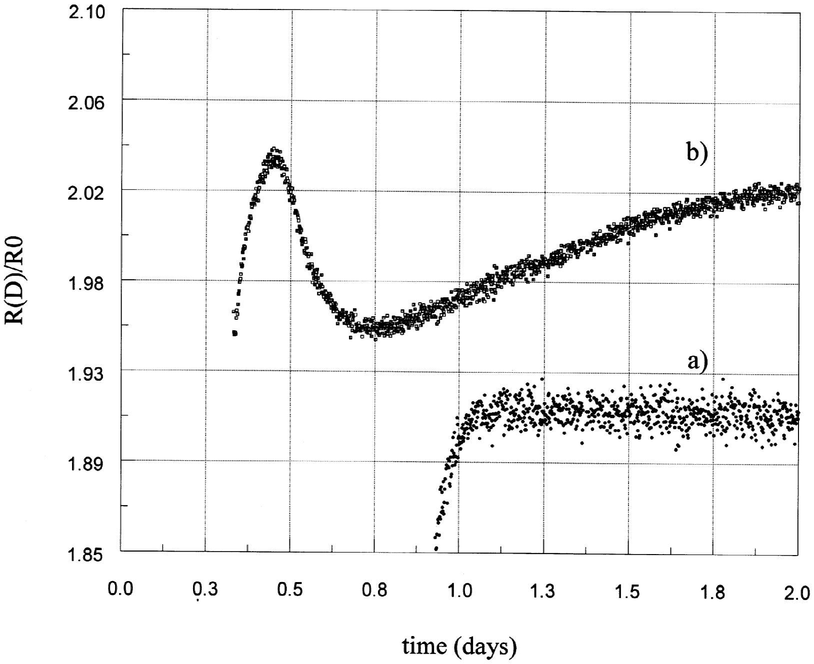

Fig. 1. (a) Pd rod loaded only by electrolysis $I=10$ mA; (b) Pd rod preloaded in D_2 gas and electrolysed, $I=10$ mA. The starting time is the same for the two samples.

and β phases: the temperature and pressure were increased over the critical values ($T_c=270$ °C and $p_c=34$ atm) and kept above the critical point for long enough to effectively ensure complete diffusion.

The Deuterium concentration, c, was monitored by measuring the electrical resistance ratio of the sample, $R(D)/R_0$, and then relating the two with an empirical correlation [3,4]. The resistace variations were measured using a four-wire technique and a lock-in amplifier at 100 Hz modulation and 2 mA excitation current.

Fig. 1 shows the comparison between (a), a sample loaded only by electrolysis in heavy water, and (b), a sample preloaded with D_2 gas and then electrolyzed. The latter shows a higher concentration value and a different loading dynamic because ofthe different loading procedure.

3. Concentration measurements: Interpretation of experimental R/R_0 ratio

Solving Eq. (2) without the stress field terms we obtained the concentration profile inside the cathode. The solution was obtained both using a centred difference approximation and a Runge–Kutta IV order method without any significative differences. The solution was obtained with the following initial and boundary condition:

$$\text{i.c.}\quad t=0,\ c=0\forall r\ \text{ or }\ c=0.65\forall r\ \text{(for the two cases)}$$

$$\text{b.c.}\quad r=a,\ c=c_s;\ r=0\ \frac{\partial c}{\partial r}=0$$

where a is the elecrode radius and c_s is the surface concentration.

The resistivity of Pd vs. deuterium can be obtained by interpolating data from the literature [3,4] with two polynomial approximations, because the R/R_0 vs. concentration is a biunique relation. We obtained that way a simulation of the behaviour of the measured R/R_0 in the case of cylindrical geometry. The electrode was dissected into ten equally spaced concentric hollows cylindrical elements, each 0.1 mm thick. The concentration in each of those slabs was assumed to be uniform for each time step. The electrical resistance was the parallel of the resistances of the cylindrical areas i.e.:

$$\frac{1}{R}=\sum_i\frac{1}{R_i}\quad i=1,2,.....10, \tag{4}$$

so that the expected experimental R/R_0 ratio can be plotted.

Two different experimental conditions were analyzed: (a) an internal force limits deuterium diffusion inside the metal and the concentration is stopped for $c=0.62$ (Fig. 2); (b) the evolution of the concentration is well described without any constrain to the Fick's law (Fig. 3). The agreement between the simulation and experiment (cf. Fig. 1) indicates that by avoiding the coexistance of $\alpha+\beta$ phase the blocking force is effectively reduced. It must be noted that a different trend in R/R_0 vs. time is to be expected for the two cases. In the first there is no maximum in the curve. The second exhibits an overshoot after the initial rise. Such effect is due to both the combined effect of the contributions from the different

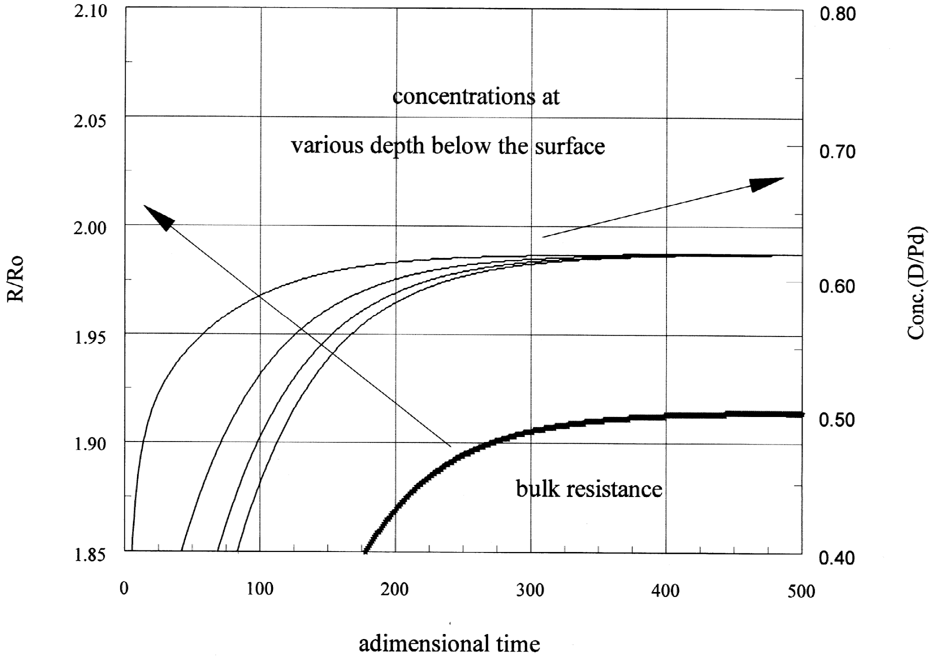

Fig. 2. Concentration limited to $c=0.62$ D/Pd.

internal slabs resistances and the behaviour of the R/R_0 vs. concentration curve that has a maximun for $c \cong 0.75$.

Internal profiles also affect the R/R_0 maximum value.

4. Discussion

These preliminary results led us to conclude that the self-stress due to the solute ion inside the palladium limits the maximum obtainable concentration.

The self strain field due to a very steep concentration gradient could be responsible for the well known difficulty in obtaining reproducible high loading samples. Furthermore, possible damages induced by the loading itself can modify the material making the process irreproducible. It also follows that a very important role is played by the initial metallurgical state of the sample.

It was experimentally confirmed that the strain field blocking force is minimised when the correct path is followed on the p–$c(D)$–T diagram.

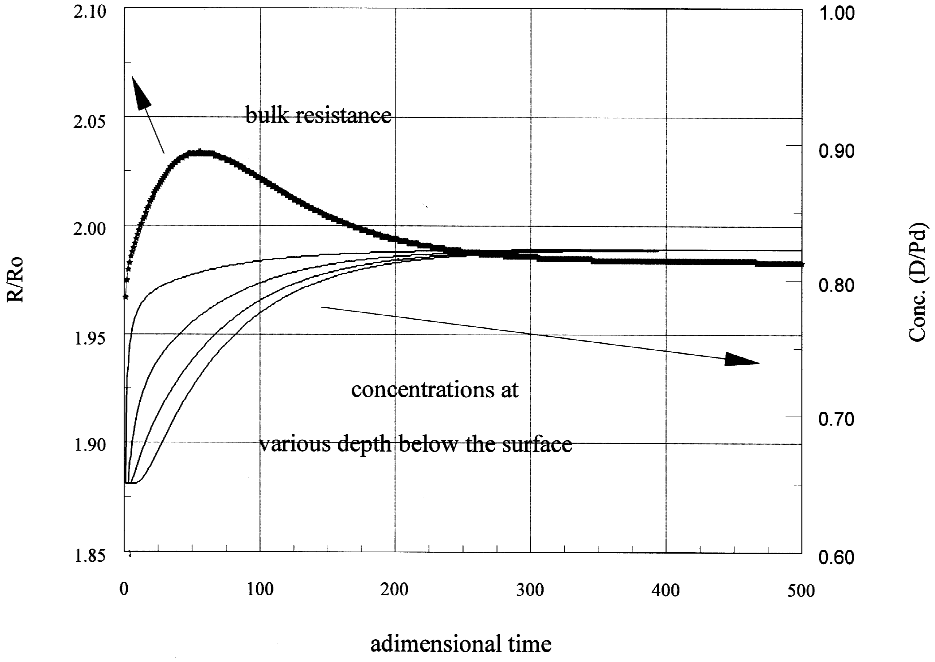

Fig. 3. Standard Fick's law diffusion model. Initial value was assumed $c_0=0.65$ D/Pd.

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