METALLURGICAL EFFECTS ON THE DYNAMIC OF HYDROGEN LOADING IN Pd

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ABSTRACT

A theoretical work based on computer modeling is presented in order to explain the difference on the hydrogen electrochemical loading dynamics for two shapes of palladium cathodes. Pd foils and wires have been investigated solving the transport equations, in order to study the effect of self stress propagating. The results allow us to study the influence of the stress relaxing (via dislocation slipping) on the loading process.

1. INTRODUCTION

Diffusion of Hydrogen in a metallic lattice is strongly affected by self stresses that arise from the movement of protons across the interstitial sites. From the irreversible thermodynamics processes point of view this phenomena can be regarded like the effect of an "additional" driving force for mass transfer due to field of stress.

Our goal is to study the different features of the diffusion of hydrogen in palladium cathodes having plane and cylindrical shape. In the experiments the loading of thin foils and thin wires is done by electrolysis. Substantial differences arises from different stress relaxing mechanism in the two considered geometries.

2. MODEL

We consider axial symmetric diffusion across a thin plate and a thin wire where the dimension along which occurs the diffusion process is of some order of magnitude less than others, so that one may describe the problem like a one dimensional system.

The chemical potential (c.p.) of the hydrogen dissolved in the lattice is modified by the stress field according to:

$$\mu(\sigma,n) = \mu_o + RTu_\beta n + RT \ln\left(\frac{n}{1-n}\right) - V\sigma \qquad (1)$$

where the first term in the right side of Eq.(1) is the standard c.p., the second one is due to the H-H interaction with the lattice, the third term is the configurational contribution and the last one is due to the stress.

The flux of Hydrogen under self stress conditions can be written [2]

$$J = -\frac{D_o\Gamma_b}{RT}n(1-n)\nabla\mu(\sigma,n)$$

(2)

where n is the atomic H/Pd ratio, the term (1-n) is the blocking factor and σ is the trace of the stress tensor. To relate the stress to the concentration field we impose the analogy with thermal stresses [4],[5] , by taking advantage of the analogies $\alpha\leftarrow\rightarrow V$ and $\Delta T\leftarrow\rightarrow\Delta n$.
The trace of the stress tensor in cylindrical and planar geometry is

$$\sigma_r = \sigma_{rr} + \sigma_{\theta\theta} + \sigma_{zz} = -\alpha\left\{\Delta n - 2\int_0^1 \Delta n\rho d\rho\right\}$$

$$\sigma_x = \sigma_{yy} + \sigma_{zz} = -\alpha\left\{\Delta n - \int_0^1 \Delta n dx\right\}$$

(3)(*)

where $\alpha = \dfrac{2V^2Y\Gamma_b}{3RT}$ and Γ_b is the maximum number of available sites for hydrogen in the lattice. We can see that stress propagation depend on the overall concentration field.
The equations for the fluxes can be substituted in the mass balance equation, leading to

$$\frac{\partial n}{\partial \tau} = -\frac{\partial}{\partial x}\left\{[1+(\alpha + u_\beta)n(1-n)]\frac{\partial n}{\partial x}\right\} \qquad \text{(foil)}$$

(4)

$$\frac{\partial n}{\partial \tau} = -\frac{1}{\rho}\frac{\partial}{\partial \rho}\left\{\rho[1+(\alpha + u_\beta)n(1-n)]\frac{\partial n}{\partial \rho}\right\} \qquad \text{(wire)}.$$

(5)

These PDE,s can be solved using suitable boundary conditions. Although Zhang et .al. [1] demonstrated that step wise increasing concentration at the cathodic surface it is not a practical situation. Here, for the sake of simplicity, one considers valid this assumption so that the B.C. become

$$\left.\frac{\partial n}{\partial x}\right|_0 = \left.\frac{\partial n}{\partial \rho}\right|_0 = 0$$

$$n(1,\tau) = 1$$

(6)

The equations were discretized for both planar and cylindrical cathodes with the method of lines, and integrated in time with a four order Runge-Kutta method.

3. RESULTS AND DISCUSSION

Fig (1) shows the evolution of dimensionless self stress field for the two different shapes at different times. It turns out that self stresses do not relax completely asymptotically.
In both cases the stress, at short times and in wide regions near the surface and near the symmetry axis, exceeds the yield stress ($\sigma = 0.11\div0.28$) , so that we can have plastic flow or dislocation slipping to release the stress. This phenomenon is more pronounced for cylindrical cathodes than for foils near the symmetry axis. So that one may assume a better stress relaxing in thin wires than in foils and as consequence an higher loading in cylindrical geometry.

The distance between the symmetry axis and the neutral axis of the stresses, is greater for the cylindrical shape than for the planar one. This effect is created by the different propagation of the stress field. For cylindrical shape we observe the effect of the "weighting" term ρ in the stress/concentration integral relationship (*).

As a matter of fact if one considers a slab of thickness δ from the symmetry axis, for both the foil and the wire, it turns out that the volume of such a region is larger in the foil case. This is due to the assumption of a foil having one dimension much smaller than the others.

Then we have more pronounced self stress field in cylindrical case. Consequently the neutral axis of the stress field is shifted towards the surface for the elastic equilibrium to be conserved.

This situation produces a small effect on the loading between wires (see fig.2) and foil having the same characteristic dimension.

The control of the stress field, by means of a proper metallurgy, leads a remarkable increasing of hydrogen solubility, as shown in fig.3.

The situation can be different if one considers the surface dynamics [1] and the stress relaxing [3].
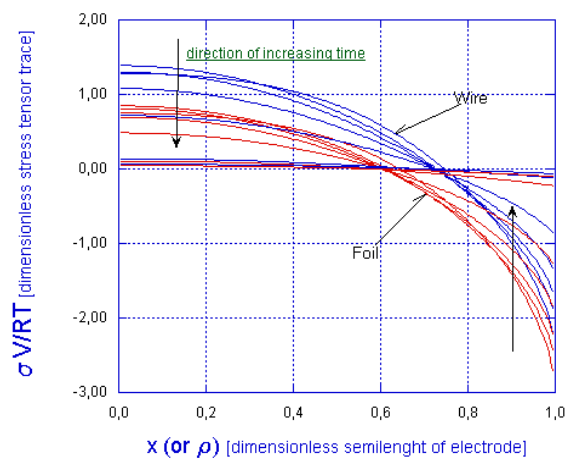

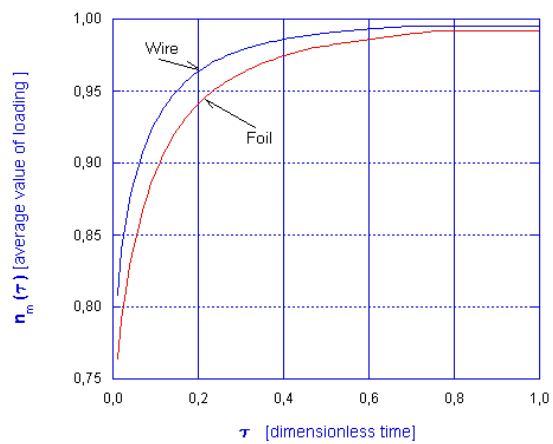Fig.1 Stress field evolution for wires and foils
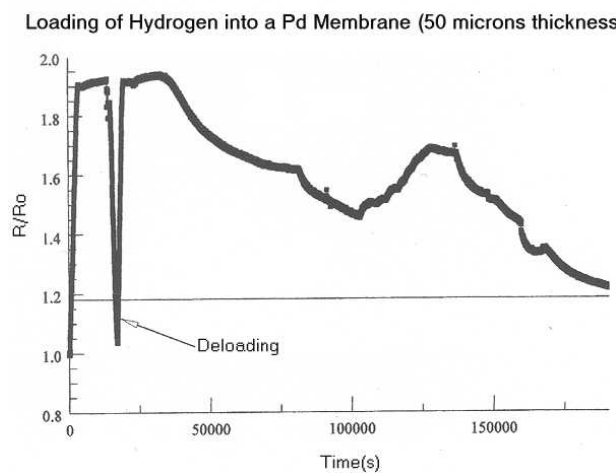

Fig.2 Average hydrogen loading evolution

Fig.3 R/Ro evolution during electrochemical loading of a Pd foil (50 μm thickness)

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