Transport Phenomena and Material Science Study Oriented to Reproducibility of High Loading of D in Pd

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Research Milestones

(1989) Announcement, by M. Fleischmann
and S. Pons, that D+D fusion
was obtained within Pd lattice.

(1991) McKubre (SRI) and Kunimatzu
(IMRA) experimentally
demonstrated that excess
power production was a
threshold phenomenon.

Miles (Naval Research Lab.)
found ^{4}He, as nuclear ash,
within electrochemical cells
giving excess power.

(1996) ENEA research activity to
increase H/D solubility in Pd.

(2003) Trigger of excess power on D loaded Pd samples by laser
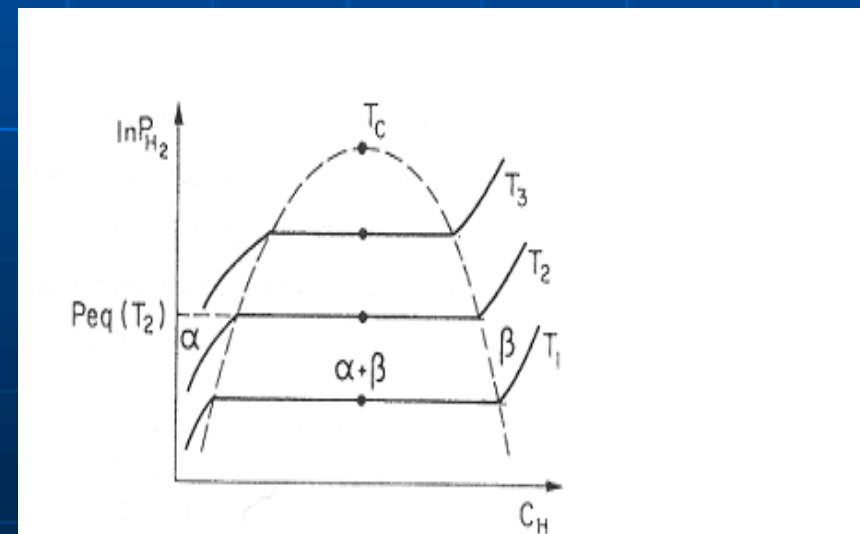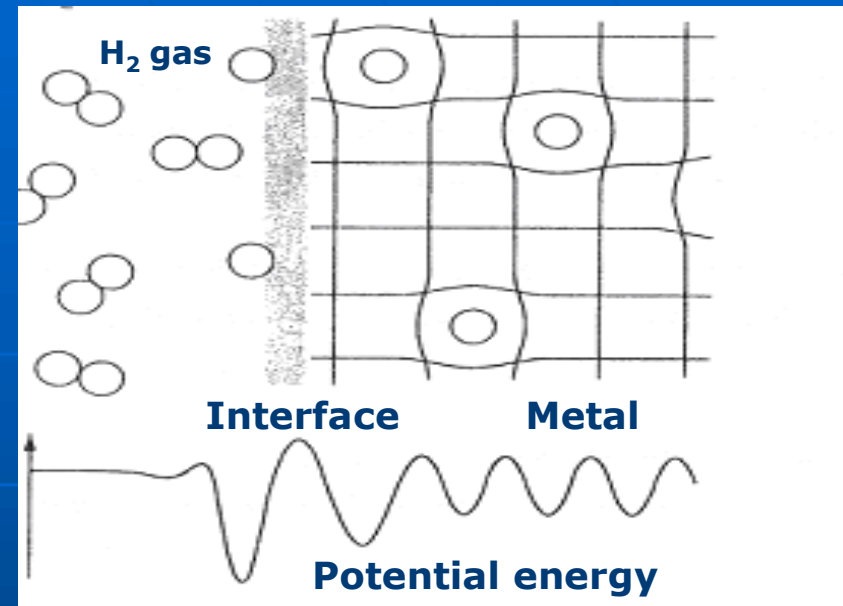
irradiation.
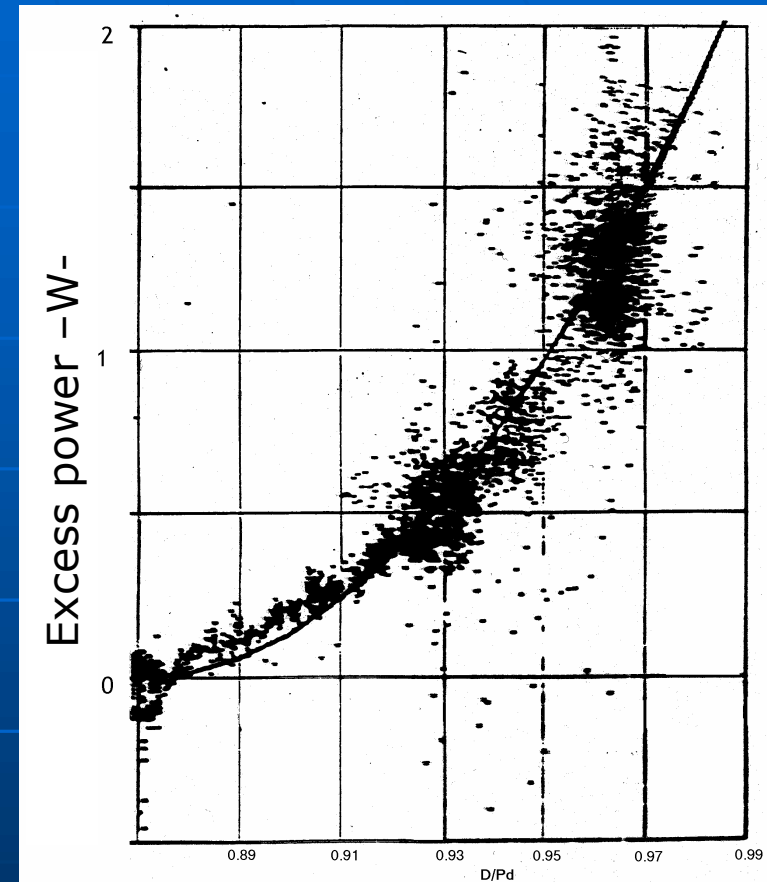
Excess power vs. concentration

Introduction

A metal hydrogen-system is composed of a metal, an interface and condensed or gas phase hydrogen.

Thermodynamics of hydrides formation is described by pressure-composition isotherms.

Under electrochemical loading the electrochemical potential replaces the hydrogen pressure (fugacity).
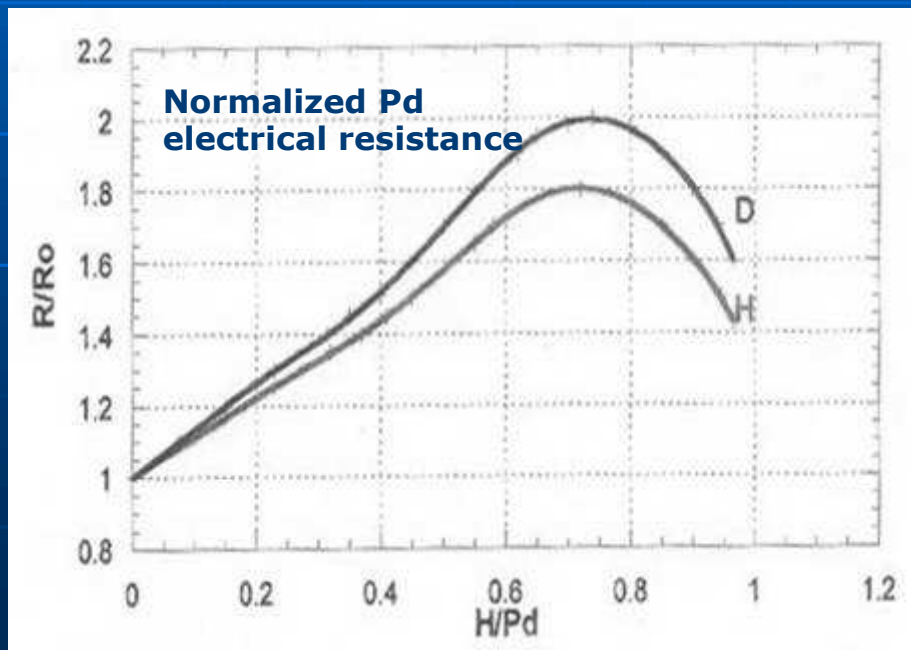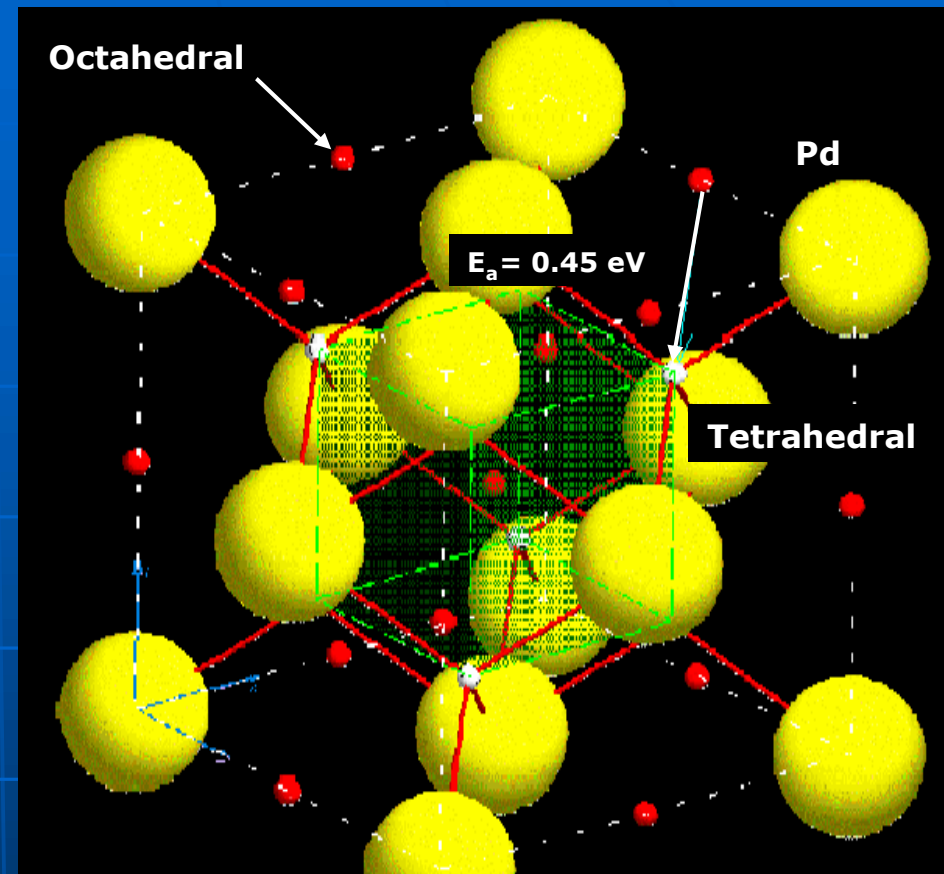

Pd-H phase diagram.

Features

Dissolution of hydrogen produces a significant elongation of the lattice parameter and a strong modification of the electronic configuration of the medium.

e.g. Pd electrical resistivity modifies with loading.

Pd-Hydride lattice cell.

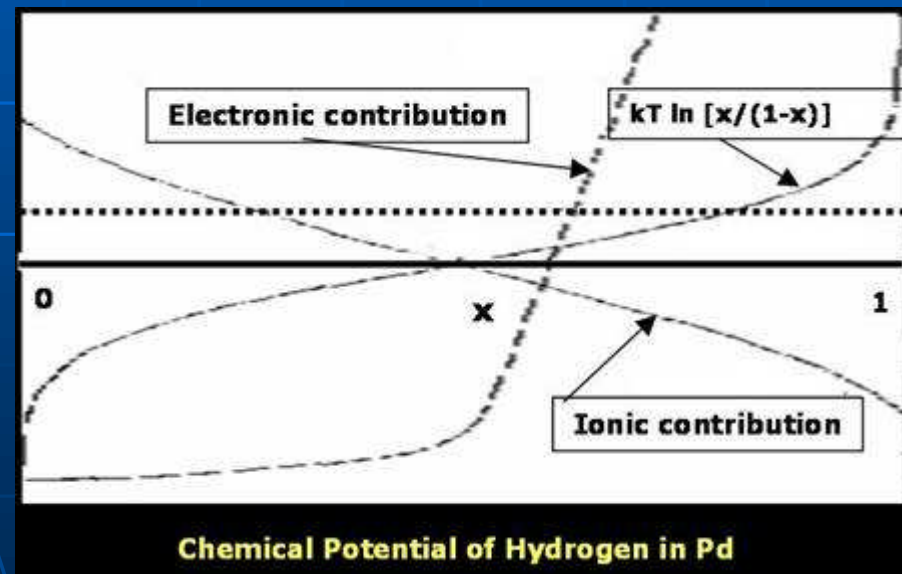Pd normalized resistance vs D/H loading.

Equilibrium and Hydrogen Isotopes Solubility in Metals

Threshold effect of excess power production leads to consider
a function able to describe the equilibrium in order to estimate if the
equilibrium concentration of deuterium is close or not to the threshold
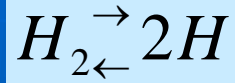one.

Chemical potential is the required function telling us how the energy of
the system increases or decreases by adding or removing one particle
respectively.

The chemical potential of hydrogen dissolved in metals like palladium is:

$$\mu_H = \mu_H^0 + RT \cdot \ln\frac{x}{1-x} + \Delta\mu_{He} + \Delta\mu_{H^+}$$

Electronic contribution

kT ln [x/(1-x)]

0

x

1

Ionic contribution

Chemical Potential of Hydrogen in Pd

Metal-Gas Phase Equilibrium

$$H_2 \underset{\leftarrow}{\rightarrow} 2H$$

The equilibrium condition is:

$$\mu_H = \frac{1}{2}\mu_{H_2}$$

Where:

$$\mu_{H_2} = \mu^0 + RT\ln(f)$$

μ_{H2} = hydrogen chemical potential at pressure P outside the metal.

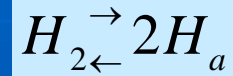f is the hydrogen fugacity:

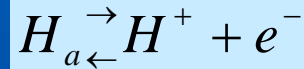$$f = \frac{p^2 V}{RT}$$

(V external volume)

Electrochemical Conditions

Hydrogen absorption within a metal lattice under cathodic polarization depends on the electrode reactions:

1) Tafel reaction:

$$H_2 \underset{\leftarrow}{\overset{\rightarrow}{}} 2H_a$$

2) Volmer reaction:

$$H_a \underset{\leftarrow}{\overset{\rightarrow}{}} H^+ + e^-$$

The associated Gibbs energy variations are:

$$-\Delta g_T = \mu_{H_2} - 2\mu_H$$

$$-\Delta g_V = \mu_H - \left(\mu_{H+} + \mu_{e^-}\right)$$

The relationship between activity and chemical potential is:

$$\mu = \mu^0 + RT \ln(a)$$

A little of algebra leads to the effective pressure under electrochemical loading:

$$P_{H_2} = \exp\left(-\frac{2mf\eta}{m+2}\right)$$

(up to 10^6 atm)

Where:

$$m = \frac{\Delta g_T}{\Delta g_V}$$

and

$$f = \frac{F}{RT}$$

Electrochemical technique results to be advantageous in loading metals with hydrogen since it prevents from working with gas hydrogen at high pressure .

Not Equilibrium Processes and Transport Phenomena Controlling Loading and Excess Power Production Reproducibility within Deuterated Metals

Absorption of hydrogen isotopes inside a metal lattice is both an equilibrium problem and a not - equilibrium one since a diffusive mass transfer process occurs during loading.

These two aspects are strongly linked since equilibrium is achieved when chemical potentials of hydrogen in the metal and in the external phase are equal and since diffusive process is generated by a chemical potential gradient.

Chemical potential of hydrogen in the metal lattice is strongly affected by the force fields that modify the free energy of the system.

Hydrogen entering the lattice produces a significant elongation of the lattice parameter. The entity of the elongation depends on the hydrogen concentration, so that a concentration gradient produces a stress field because regions at lower concentration of hydrogen exert a compression on the regions at higher concentration where the elongation is larger.
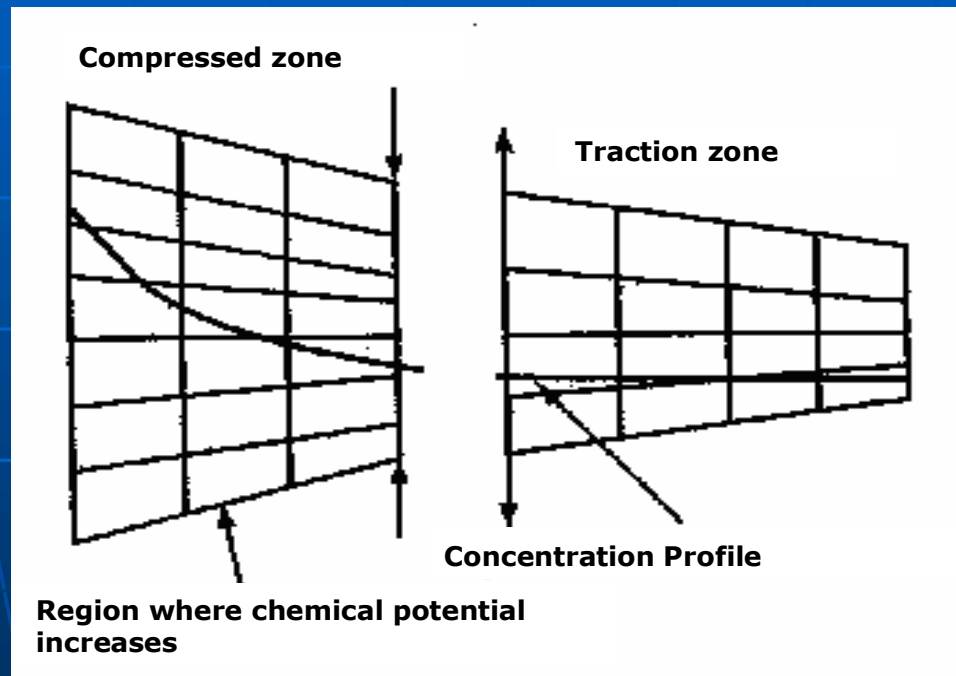
Effect of the hydrogen concentration profile on the stress field.

In presence of stress the chemical potential of an interstitial solute is correlated to the chemical potential without stress by (R. Oriani, Proc. ICCF-4):

$$\mu_s - \mu_s^* = \sum_i \sum_j \int_0^{\sigma_l} \left[V_m s_{ij} + (1 - x_s) V_m \frac{\partial s_{ij}}{\partial x_s} \right] \sigma_i d\sigma_j - V_m (1 - x_s) \sum_i \sigma_l \frac{\partial \varepsilon_i}{\partial x_s}$$

If the Young module E $> \sigma$ the first term on the right side may be neglected, terms out diagonal are neglected since the elongation is isotropic so that:

$$\mu_s = \mu_s^* - \frac{V_s}{3} \left(\sigma_{xx} + \sigma_{yy} + \sigma_{zz} \right) = \mu_s^* - V_s tr\overline{\overline{\sigma}} \equiv \mu_s^* - V_s \sigma_h$$

V_s is the solute molar volume, μ_s^* is the chemical potential if $\sigma = 0$.
The flux equation with a force field is:

$$\overline{J} = -Mc\nabla\mu + Mc\overline{F}$$

In terms of local stress, some algebra gives:

$$\overline{J} = -D(\nabla c - \frac{c\overline{V}_s}{RT}\nabla\sigma)$$

The zero flux condition:

$$J = -D(\nabla c - \frac{c \overline{V}_s}{RT} \nabla \sigma) = 0$$

allows us to estimate the order of the stress able to inhibit the diffusion:

$$\Delta \sigma \cong 1.5 \times 10^{10} \quad dyne/cm^2$$

less than values existing in lattices.

It turns out that stress field, typically created in lattice, can have a dramatic effect during hydrogen loading within a metal lattice.

Considering that

$$\sigma = E\varepsilon$$ where $$\varepsilon(\overline{c}) = [1 + b(\overline{c} - \overline{c}_{\beta \min})]$$

and by introducing the following dimensioless parameters

$$\overline{x} = \frac{x}{L} \; ; \; \tau = \frac{L^2}{D}$$
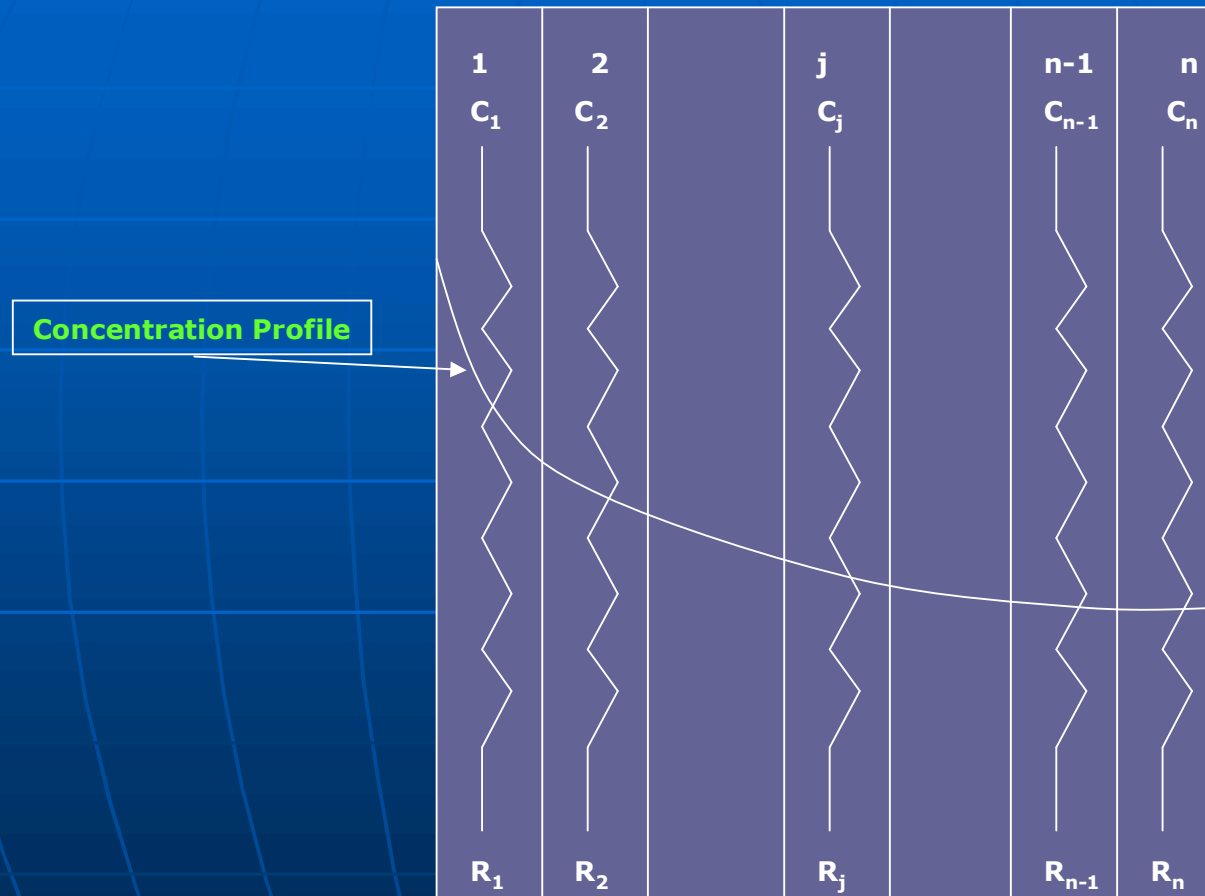
the transport equation becomes:

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$$\frac{\partial \bar{c}}{\partial \tau} = \frac{\partial^2 \bar{c}}{\partial \bar{x}^2} - (1-\eta)b\frac{\bar{V_s}E}{RT}\left(\frac{\partial \bar{c}}{\partial \bar{x}}\right)^2 - (1-\eta)b\frac{\bar{V_s}E}{RT}\bar{c}\frac{\partial^2 \bar{c}}{\partial \bar{x}^2} - b\frac{\bar{V_s}E}{RT}\frac{\partial \eta}{\partial \bar{x}}\bar{c}\left(\frac{\partial \bar{c}}{\partial \bar{x}}\right)$$

η is the percentage of relaxed stress, locally it may be roughly estimated as:

$$\eta = \frac{\sigma_{loc}}{\sigma_{sn}}$$

$$\sigma_{loc} = \delta \varepsilon E$$

Finite Difference Mesh

Elements of the domain as resistances in parallel.

Initial and boundary conditions are:

$$\overline{c} = 0 \quad \overline{x} > 0 \quad t = 0$$

$$\overline{c} = 1 \quad \overline{x} = 0 \ (\overline{r} = 0) \ \forall \ t$$

and

$$\partial \overline{c} / \partial \overline{x} = 0 \, (\partial \overline{c} / \partial \overline{r} = 0) \qquad \overline{x} = L/2 \ \forall \, t$$

For cylindrical geometry one has:

$$\frac{\partial \overline{c}}{\partial \tau} = \frac{1}{\overline{r}} \frac{\partial}{\partial \overline{r}} \left(\overline{r} \, D \, \frac{\partial \overline{c}}{\partial \overline{r}} - \overline{r} D \alpha (1 - \eta) \overline{c} \, \frac{\partial \overline{c}}{\partial \overline{r}} \right)$$

$$\alpha = \frac{\overline{V} \, E \, b}{R \, T}$$

References

A.De Ninno, V. Violante et Al., Consequences of Lattice Expansive Strain Gradients on Hydrogen Loading in Palladium. Phys. Rev. B, Vol. 56, N. 5 (1997) 2417-2420.

A. Adrover, V. Violante et Al. Stress induced diffusion of hydrogen in metallic membranes, Cylindrical vs. planar formulations I, J. Of Alloys and Compounds I(2003).

A. Adrover, V. Violante et Al. Stress induced diffusion of hydrogen in metallic membranes, Cylindrical vs. planar formulations II, J. Of Alloys and Compounds I(2003).

A. Adrover V. Violante et Al. Effects of self-stress on hydrogen diffusion in Pd membranes in the coexistence of α and β phases. J. of Alloys and Compounds II (2003).
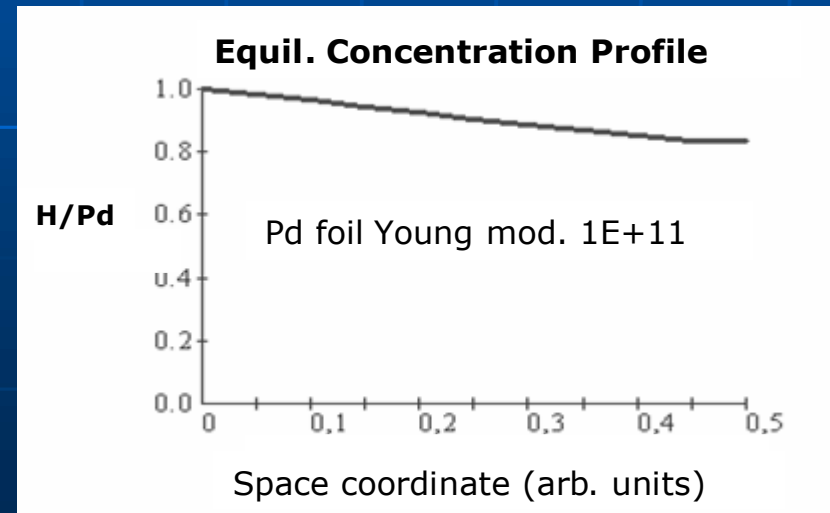
Calculations Results
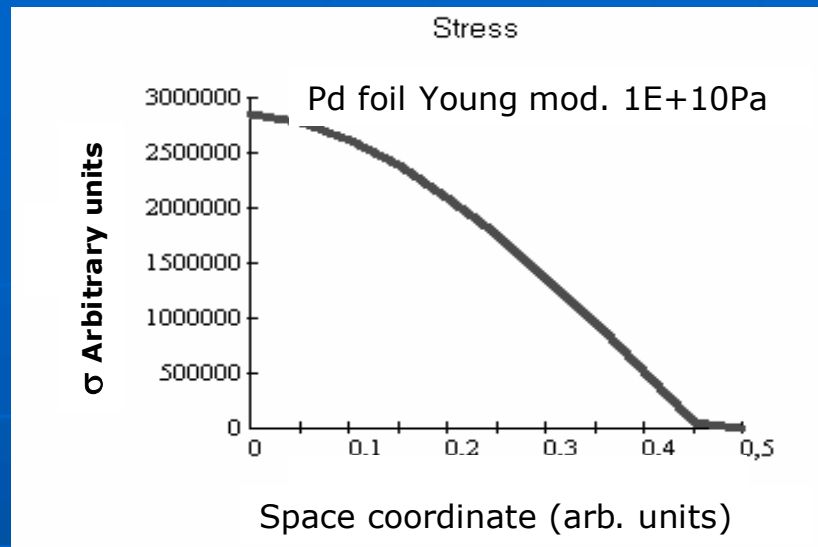
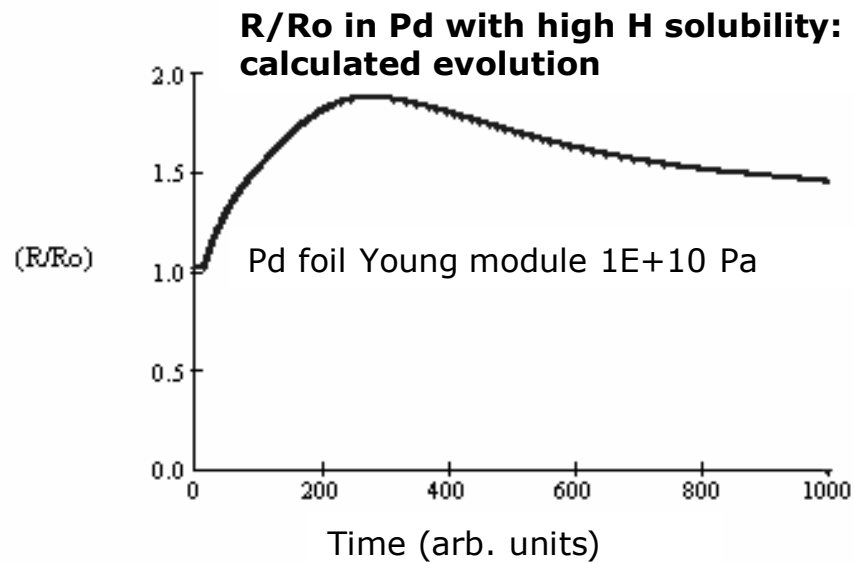Equilibrium stress profile for high H solubility in Pd.
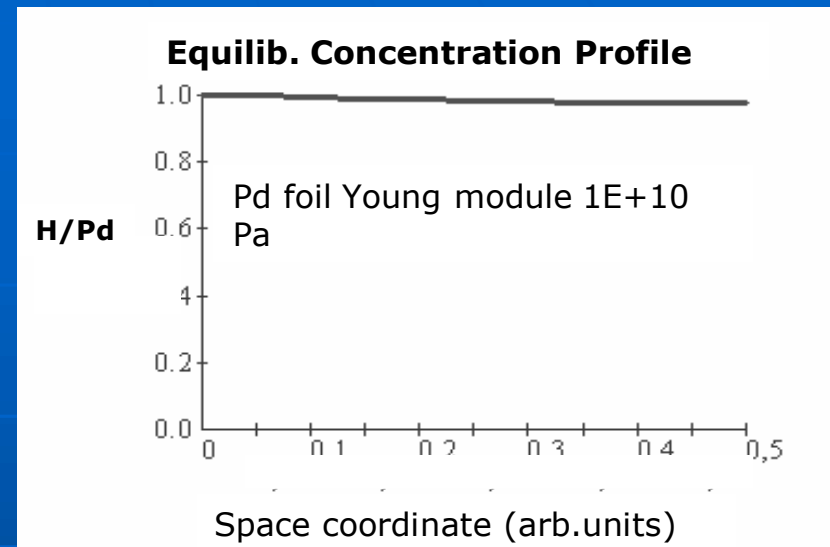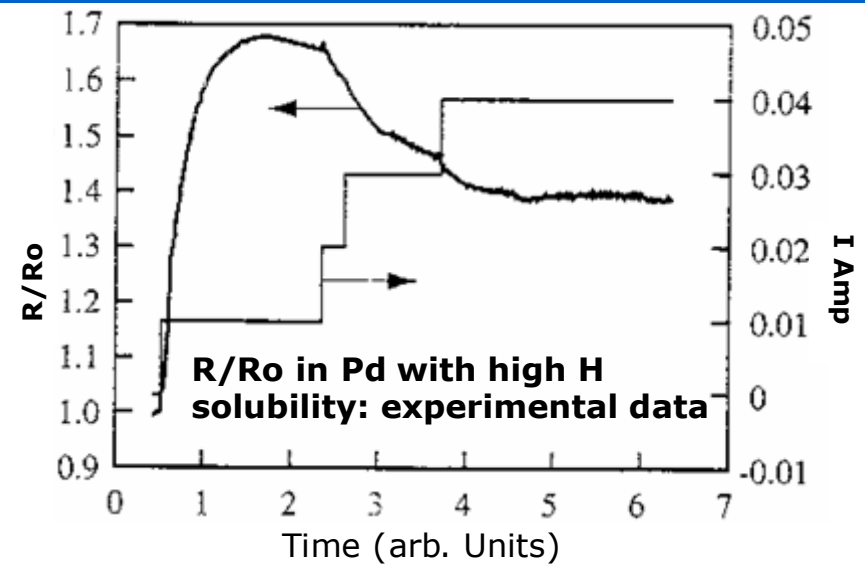

Equilibrium conc. profile for high H solubility in Pd.
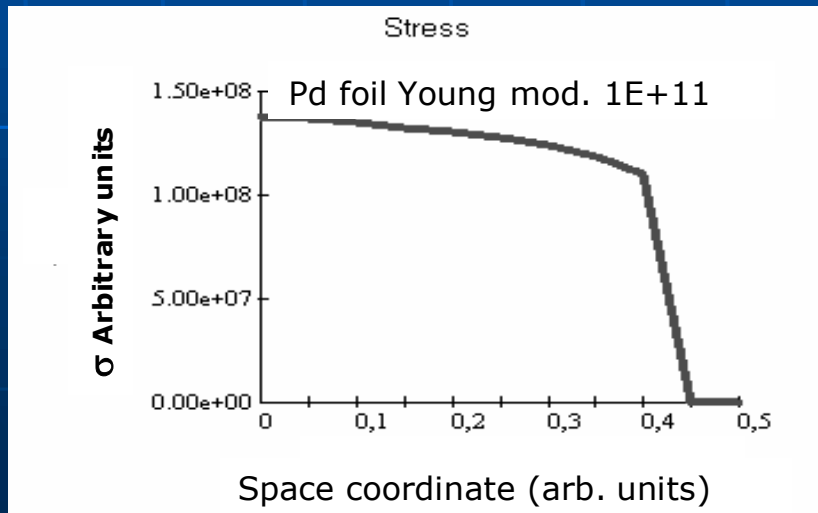
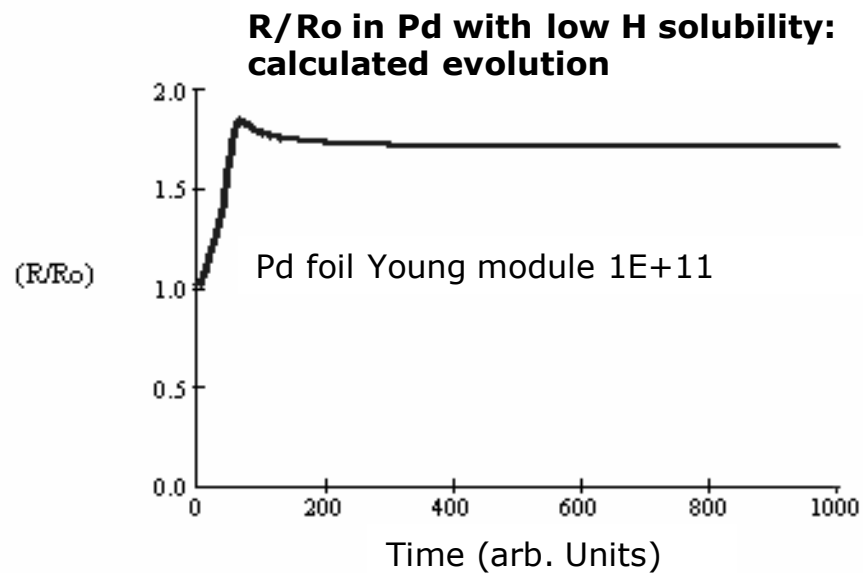Equilibrium stress profile for low H solubility in Pd.
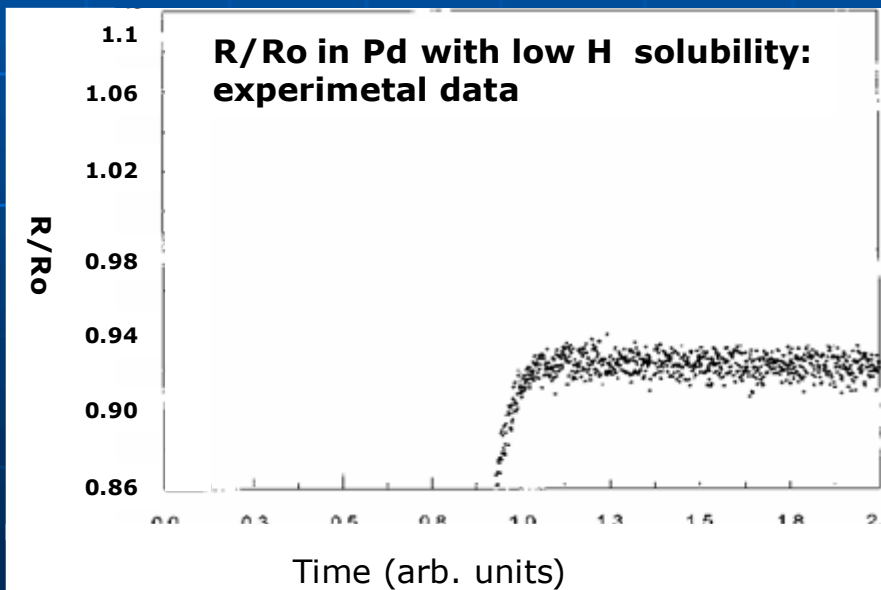

Equilibrium conc. profile for low H solubility in Pd.

R/Ro in Pd with high H solubility: calculated evolution

Pd foil Young module 1E+10 Pa

(R/Ro) — Time (arb. units)

Calculated evolution of R/Ro for high H solubility in Pd.

R/Ro in Pd with high H solubility: experimental data

R/Ro — I Amp — Time (arb. Units)

Experimental evolution of R/Ro for high H solubility in Pd.

R/Ro in Pd with low H solubility: calculated evolution

Pd foil Young module 1E+11

(R/Ro) — Time (arb. Units)

Calculated evolution of R/Ro for low H solubility in Pd.

R/Ro in Pd with low H solubility: experimetal data

R/Ro — Time (arb. units)

Experimental evolution of R/Ro for low H solubility in Pd.

Grain Boundary Effect on Mass transfer
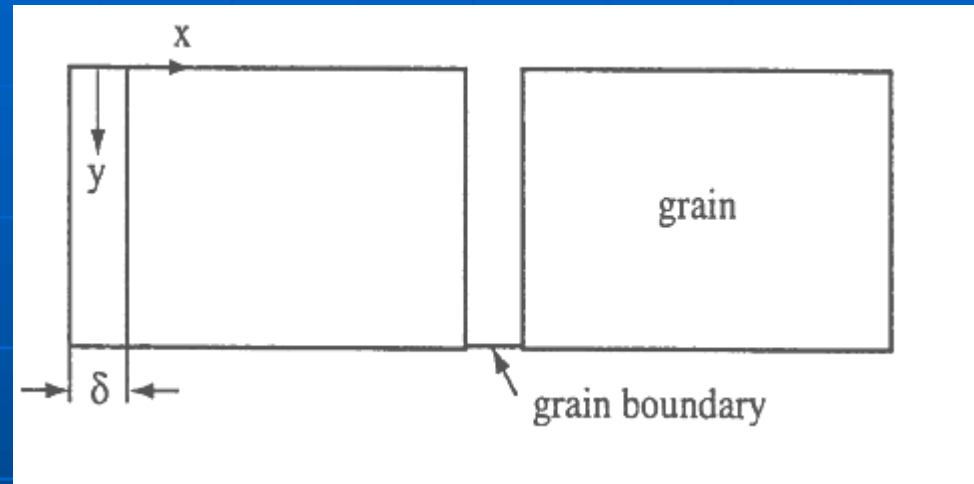
Grain /grain-boundary system scheme.

A differential mass balance yield a system of differential equations describing the mass transfer process for the grain-grain-boundary system.

$$\frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial y^2} + \frac{2D_g}{\delta}(\frac{\partial C_g}{\partial x})_{x=\delta/2}$$

Grain boundary
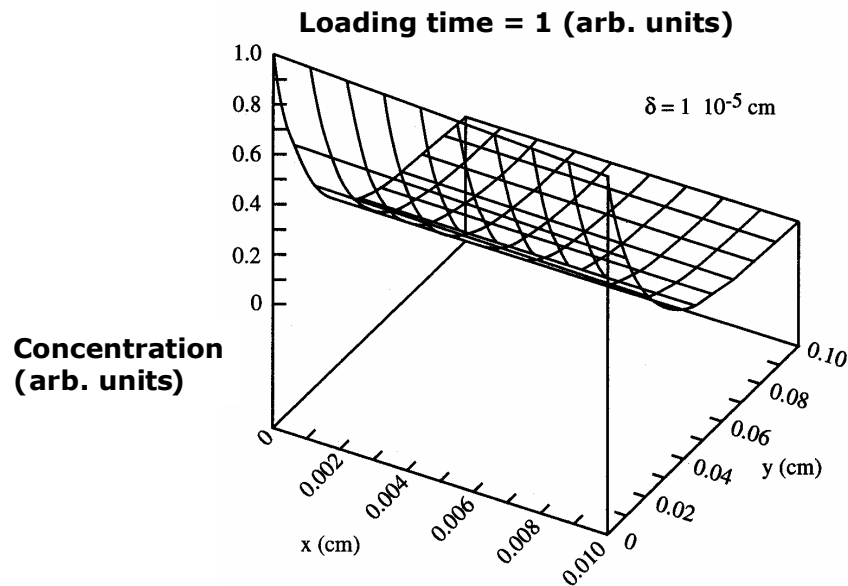
$$\frac{\partial C_g}{\partial t} = D_g \nabla^2 C_g$$

grain

IC) y=0, t=0 C=C_0; y>0, t=0 C=0
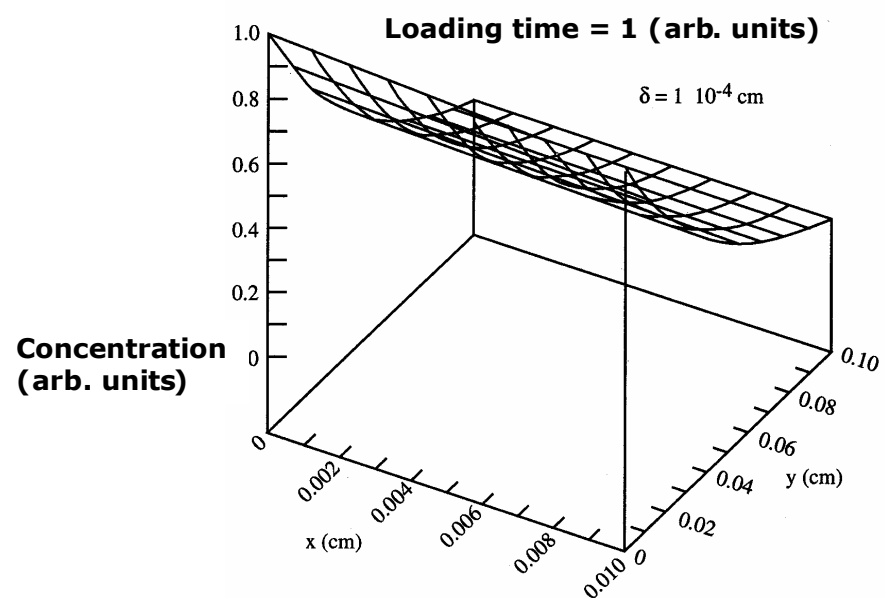BC) x=0, C_g=C_b

Solution is:

$$C_g(x, y, t) = C_0 \exp\left[\frac{-y\sqrt{2}}{\left(\pi D_g t\right)^{1/2}\left(\delta D_b / D_g\right)^{1/2}}\right]\left[1 - erf\left(\frac{x}{2\sqrt{D_g t}}\right)\right]$$

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**Concentration profile for boundary grain size of 0.1 μm.**

Concentration profile for boundary grain size of 1 μm.

The grain boundary size (or the diffusion coefficient at grain boundary) modify the transport dynamics and the diffusing hydrogen concentration profile.
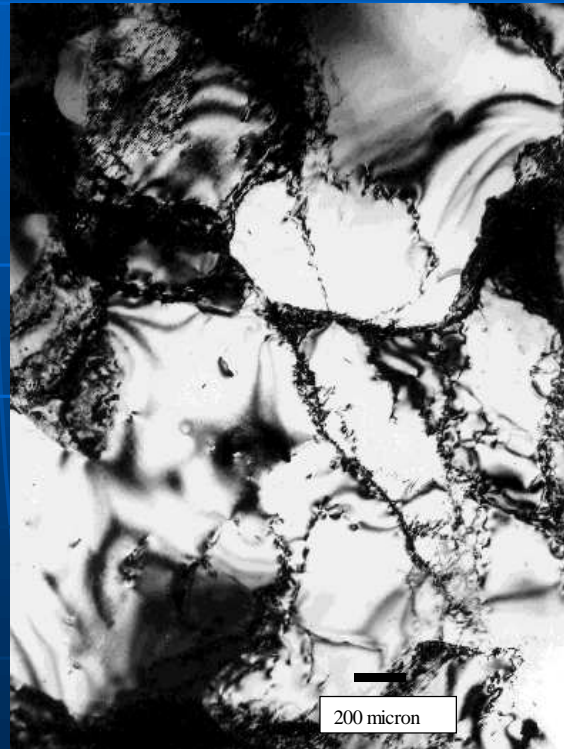
Metallurgy and Loading

The theoretical approach showed that stress fields may reduce hydrogen solubility in metals. Self induced stress field are created by all the mechanisms able to increase the concentration gradients.
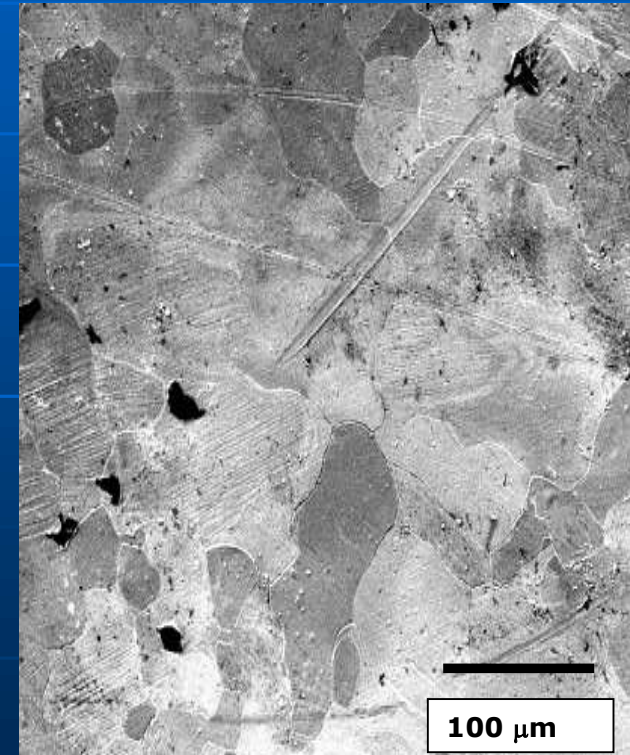
Metallurgical treatments have been studied to reduce the above mentioned effects.
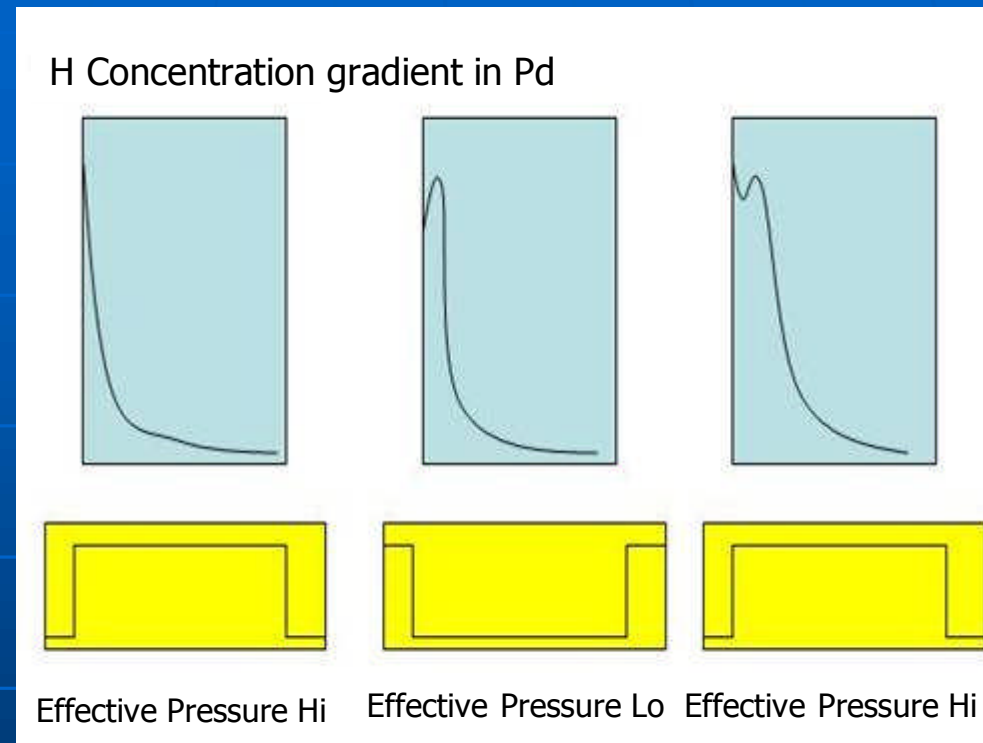

200 micron
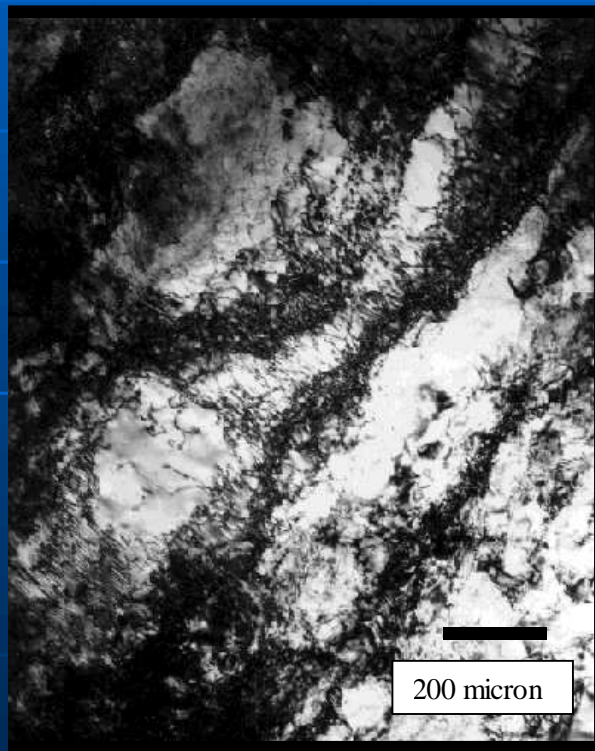
Cold worked Pd foil.

200 micron

Cold worked and annealed at 1100 °C for 5 hr Pd foil.

100 μm

Cold worked and annealed at 850 °C for 1 hr.

Loading Dynamics Effect

H Concentration gradient in Pd
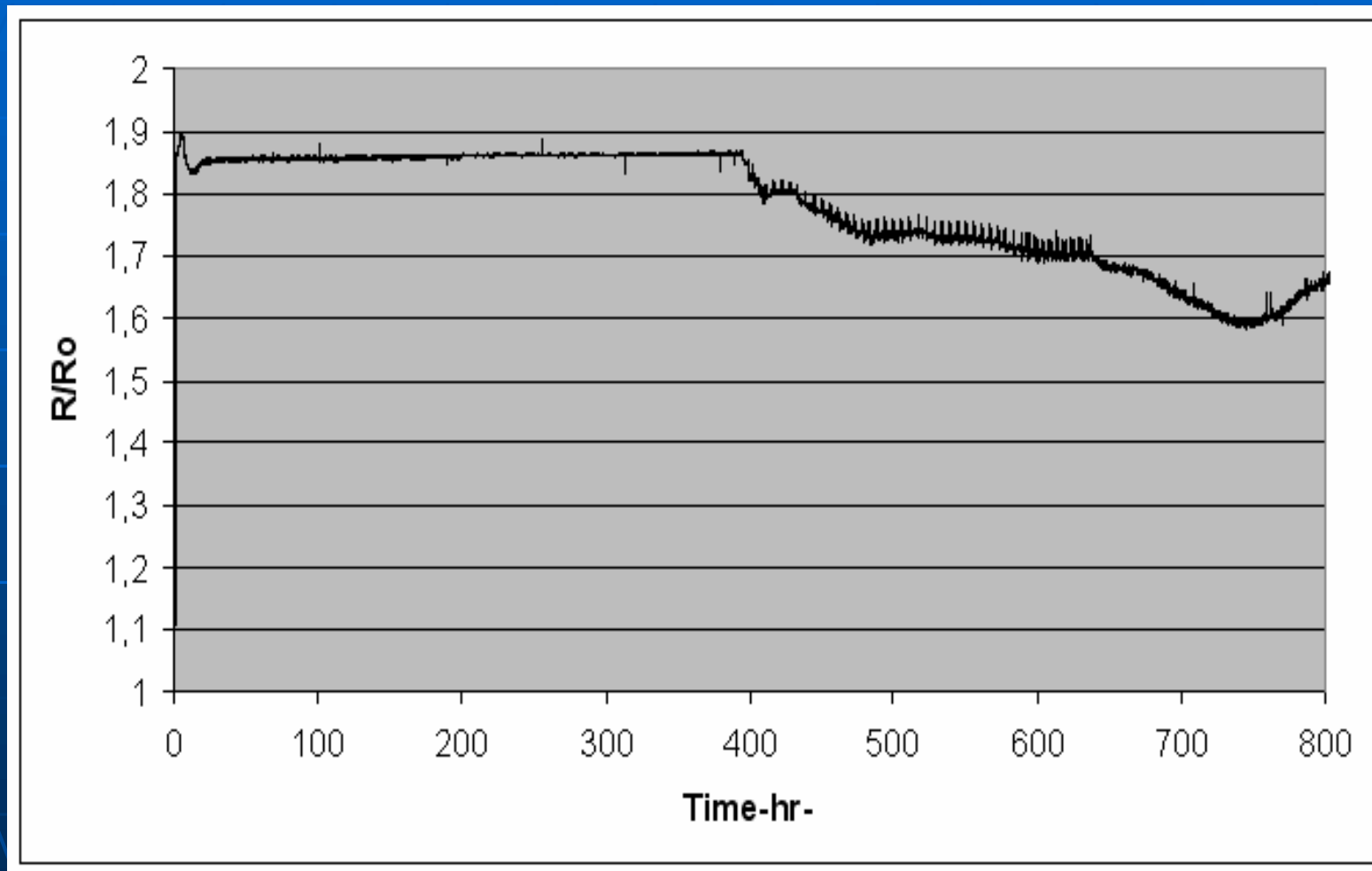
Effective Pressure Hi   Effective Pressure Lo   Effective Pressure Hi

Action of the effective pressure on the concentration gradient.

Different values of the period and of the amplitude allow to modify the concentration gradient within grains at different positions into the metal sample.

Loading Curve of Treated Palladium

**Evolution of D concentration as R/Ro.**
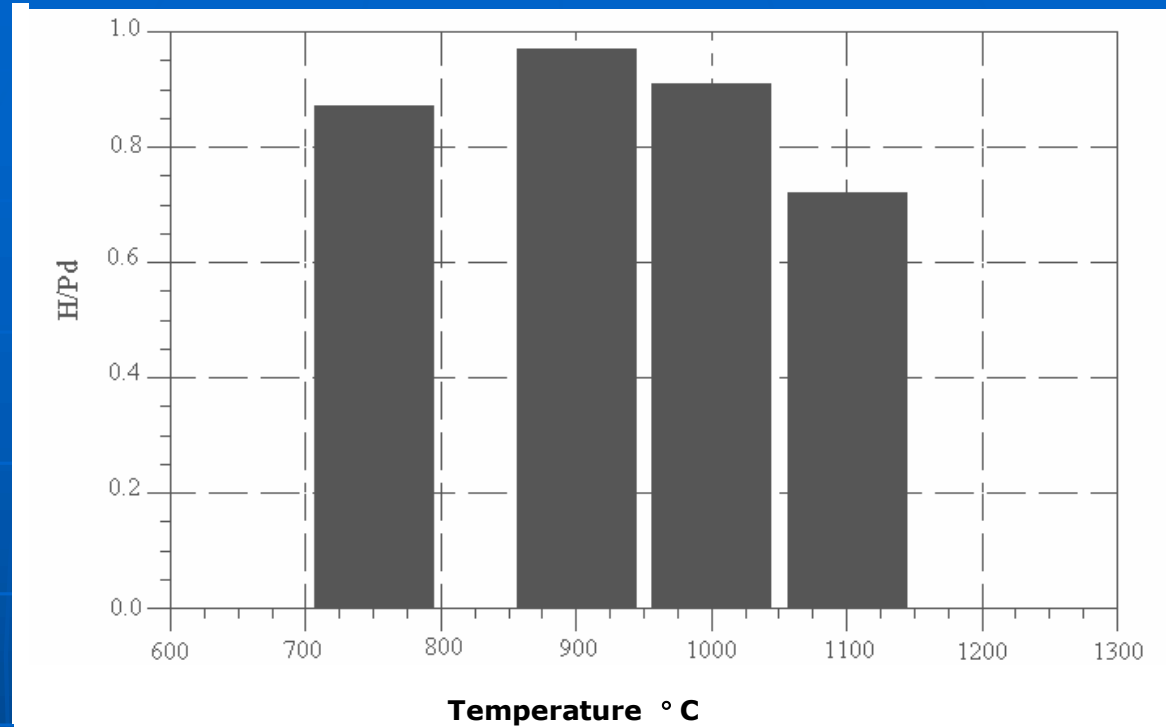
Annealing temperature effect on H loading in Pd.

A significant effect of the metallurgical treatment (then of the microstructure of Pd) comes out .

The Pd foil showing the best H solubility was undergone to electrochemical loading of deuterium within a calorimetric system with a sensitivity $\pm$ 40 mW.
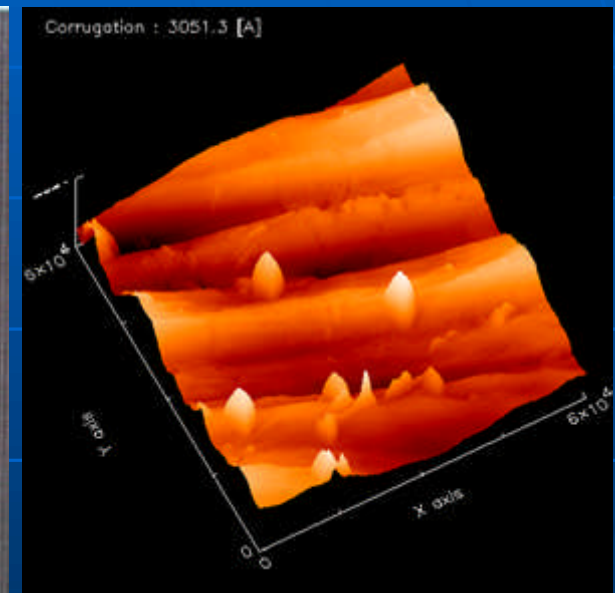
Different surface different behavior
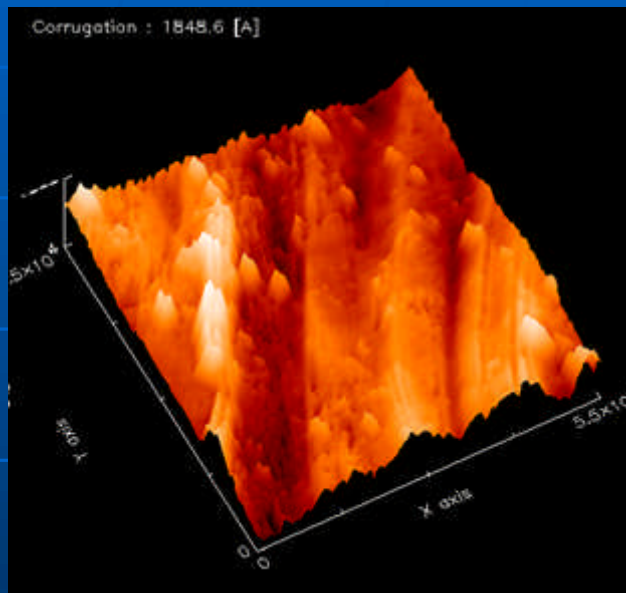
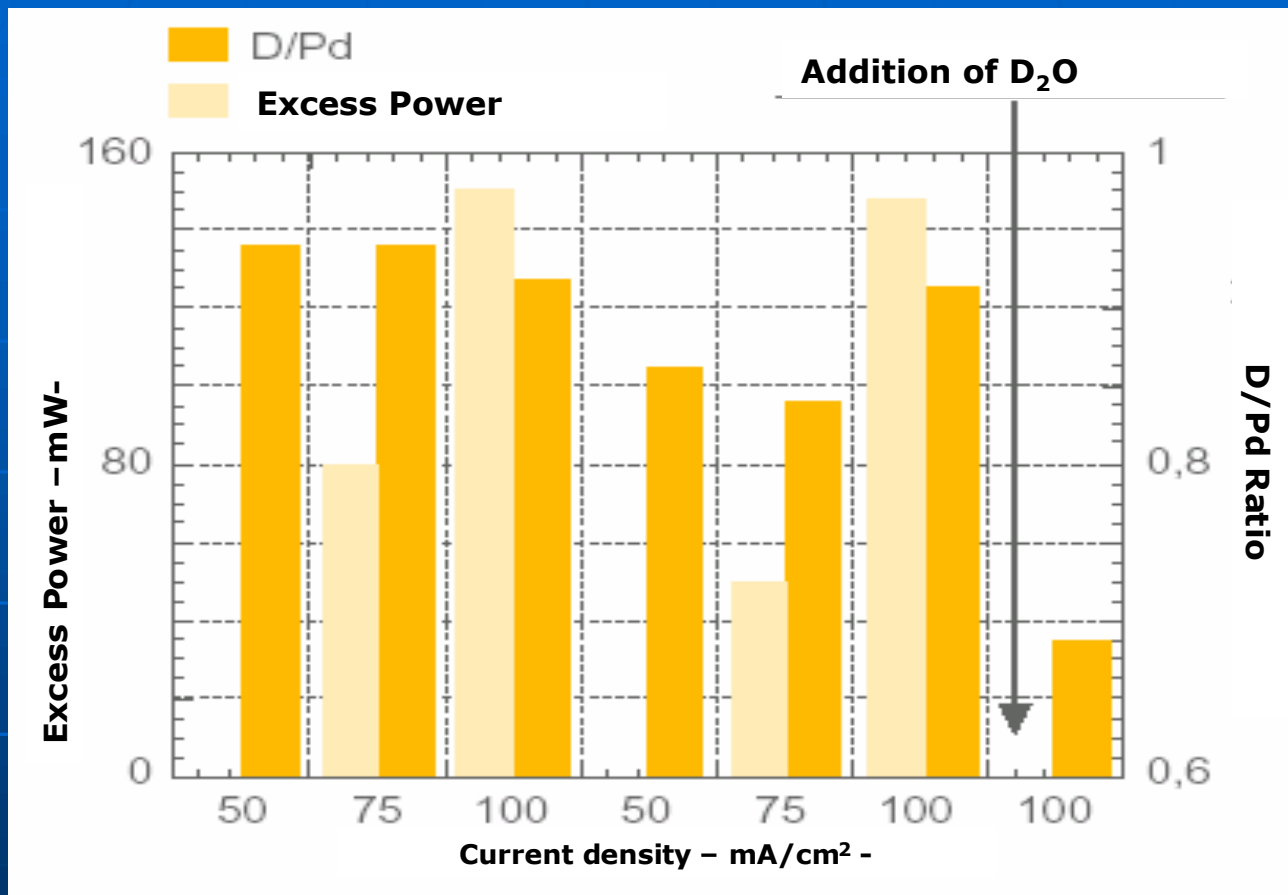Palladium giving excess, before electrolysis.

Palladium giving excess, (after electrolysis) with Pd deposition during electrolysis.

Not working palladium

L. Bertalot, V. Violante et Al. Study of Deuterium Charging in Palladium by the Electrolysis of Heavy Water. Heat Excess Production. Il Nuovo Cimento, 15, N.11 (1993) 1435-1443.

Excess Power and D Loading
vs current density.

Conclusions

The self induced strain created by very steep concentration gradients are responsible of the well known difficulty in obtaining samples characterized by high hydrogen isotopes solubility: $x > 0.95$.

A metallurgical microstructure with a proper mass transfer pathways for the solute and with the capability of relaxing the stresses (produced by the D(H) diffusion) strongly affects the loading ratio.

Loading dynamics plays a role in disturbing steep concentration gradients and helps achieve high deuterium loading in Pd.

High loading is a necessary condition to have excess power for such a threshold phenomenon.

Absence of the reproducibility of excess power production may be ascribed to the absence of high loading reproducibility.