The Effect of γ-β Phase on H(D)/Pd Overloading

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Abstract

It will be shown, using long and thin wires of Pd, that the Electromigration is a powerful tool to increase the H(D) loading in Pd only, and only if, some proper experimental set-up and conditions are fulfilled. Some of key interrelated parameters are: wire diameter, effective wire temperature, strong barriers at most and less cathodic side, anode-cathode and intercathodic voltages, current densities, proper impurities on the Pd surface, ageing effects.

PACS N.: 41.70.+t;   52.35.–g

INTRODUCTION

Since 1993 we have used the electromigration effect in order to increase the Deuterium (D) loading in Pd (plates 25x25x1mm, thin wires from 1994)[1], and to promote, *after overloading,* some strong non-equilibrium conditions. The final aim is to "generate" anomalous excess heat.

***The electromigration relation is:

$$C(x)=C_o*e^{\{[-e*Z^{\wedge}*V(x)]/(K_B*T)\}}$$ (1)

where:

Co=initial concentration of H(D); e=electron charge, $1.6*10^{-19}$C; V(x)=Voltage drop along Pd wire *supposed completely homogeneous,* $Z^{\wedge}$= effective charge of H (D) in Pd [it is 1 at low concentration (<0.6) and room temperature; it drops to 0.1 at larger concentration or temperature]; K_B=Boltzman constant, $1.38*10^{-23}$ J/K; T=Temperature (K).

***The intrinsic resistivity ρ_O of Pd, at 20^C, is 10.5 $\mu\Omega$cm and, to get the voltage drop of 1V/cm, it is necessary to feed a current density as high as 95200 A/cm^2, *supposing no self-heating effect due to current flowing* . It can be easily calculated that, with V=1V, T=300K, $Z^{\wedge}$=1 the ratio C(x)/Co (then pressure) can reach values as high as e^{39}: speculatively, it is possible to think to any kind of nuclear fusion.

We recall that the resistivity of Pd increases, according to loading increase, up to a factor of 2 with D (1.8 with H) and decreases afterward on very large loading conditions. Data allowable from open literature show that the maximum of resistance is at H(or D)/Pd=0.75 and the maximum loading ratio of about 0.97 for both H and D: the R/Ro is respectively 1.43 for H and 1.60 for D. Unfortunately, almost no data are allowable about Tritium.

***Another, strange, peculiarity of H(D)/Pd system is that the diffusion speed of H(D) changes in a remarkable way upon loading, according to the following Table 1.

Table 1 – Diffusion speed of α, β, γ, super-γ, H(D)-Pd phases.

Phase	Concentration	Diffusion speed (cm^2/s)
α	<0.1	10^{-5}---10^{-6}
β	0.1--0.75	10^{-6}---10^{-7}
γ	0.75--1.0	10^{-4}---10^{-3}
super-γ	>1	>10^{-3}(only indication)

***According to the electromigration formula, it is necessary to maximise the ratio V/T in order to increase the concentration gradient of H(D) in Pd.

The voltage drop (V), according to the Ohm law, is:

$$V=I*R=I*\rho*l/s=I*\rho*l/(\pi*r^2)$$ (2)

The *Effective Wire Temperature* (T_*ew*) depends on the ratio between the total surface area (S) and the volume (Vol.); if l>>r, we get Eq. 3:

$$T\_we=1/(\tau*S/Vol.)\sim1/[\tau*(2*\pi*r*l)/(\pi*r^2*l)]=r/(2*\tau)$$ (3)

As final result, the ratio V/T as the following expression, Eq.4:

$$V/T=[I*\rho*l/(\pi*r^2)]/(r/2)=(2*I*\rho*\tau*l/\pi)*(1/r^3)$$ (4)

where:

ρ=resistivity; l=length; s=surface of cross section; r=radius; τ=heat exchange constant.

It results that, given some material resistivity ρ *and heat exchanging constant* (τ) *of the bath where the wire is immersed, the ratio depends only on::*   **l/r^3.**

**In Fig.1 it is shown the behaviour of ratio V/T versus current flowing inside pure Pd wire (r=25μm), in pure water at 20^C.
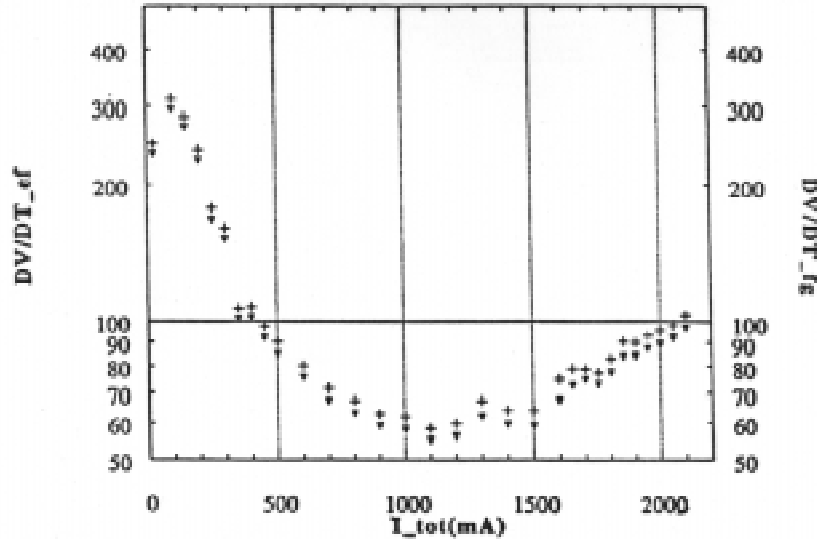
Fig. 1 – ΔV/ΔT ratio vs. electromigration current.

The V/T ratio, after increasing up to 0.1A, decreased up to 1A and later increased again only when the local temperature around wire reached the boiling point of the water (Fig. 2) Because the enthalpy of evaporation is as large as 2258.7J/g, as final effect , the heat exchange constant of water "increases" of the ratio 2258.7/4.2, then improving the V/T ratio. It is ease to predict that the minimum current necessary to enter into the "positive derivative" region decreases increasing H(D) loading (the resistance increases up to entering of γ phase) and/or increasing the bath temperature.
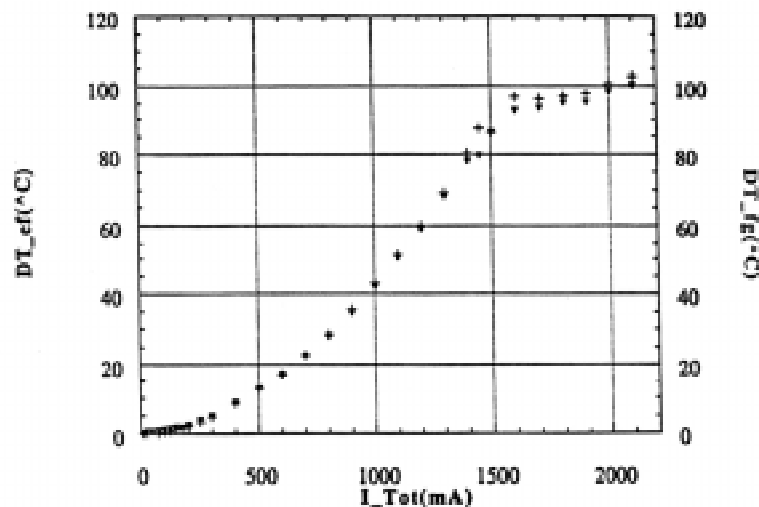

Fig. 2 – Increases of T_*we* vs current, for a bare Pd wire (r=25μm), at 20^C bath temperature.

SUMMARY OF PREVIOUS AND PRESENT EXPERIMENTS

The main information we get during the previous 6 years of experimental activity on the "generation " and the detection of anomalous excess heat, can be summarised as following:

**PULSED ELECTROLYSIS: quite reproducible excess heat; poor understanding;

**DC ELECTROLYSIS: poor excess heat; good understanding;

**when the loading ratio at Less Cathodic (LK) side of the wire reached a value larger than at Most Cathodic (MK) one, the excess heat always disappeared (Fig. 3);
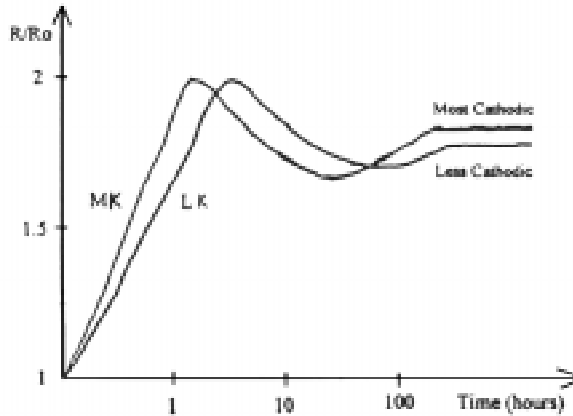
Fig. 3 – Loading ratio, vs. time (log. scale), at MK and LK sides of the wire.

** exist a "natural" (almost not stable over time) barrier at the ends of the wire due to the soldering (Pb-Sn alloy) with the Cu wire used, in our experimental set-up, to feed current;

**it is possible to build a stable, reproducible barrier at the end of the wire and its behaviour depends mainly on the T_we : its temperature can be quite different from the other section of the wire (Fig. 4);
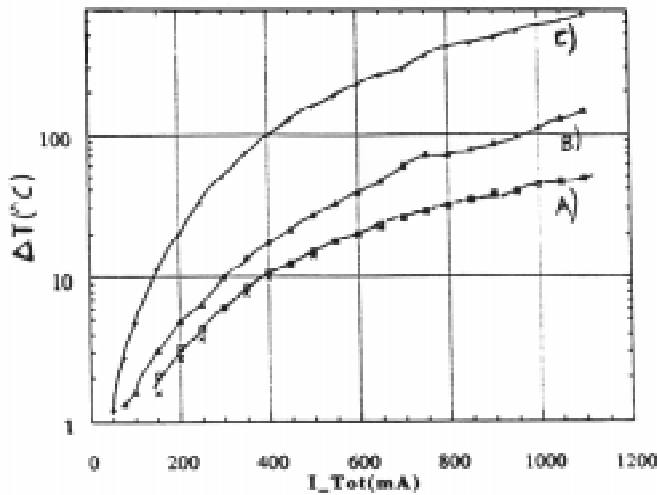
Fig. 4 – Temperature increasing of a Pd wire (r=25μm), immersed in water (20^C) in 3 different conditions: A) bare; B) covered by "electronic" thermal-conducting paste and surrounded by shrinking tube; C) surrounded only by shrinking tube.

**the value of loading on the whole wire, because combined effects of thermal diffusion (uncontrollable) and the electromigration-enhanced diffusion (controllable) depends, in a significant way, on the phase and temperature of the ends of the wire;

**the electrolysis at "high voltage" gives a final value of loading larger than that at high current;

**it exists a maximum value of electrolytic current density ($\sim0.4A/cm^2$), if it is overcame the loading saturates and over $0.6A/cm^2$ even decreases;

**the excess heat (in one of our best experimental result)[2] appeared only during fast non-equilibrium conditions at large loading ratio: because of large power value (even over 100W), large energy gain (up to 2.5), long time lasting (over 13 hours with the Researcher present

during the event) it was not an experimental error and it was impossible to be explained by only chemical reactions or energy stored in the Pd lattice (wire, r=0.05mm, l=160cm);
** it is possible, with thin wires at very large current density flowing (>60000A/cm^2), to get local boiling of the water around the wire even with a mean bath temperature as low as 20^C. This effect can simply explain the reason because, in some "promising" experiments with D_2O, the Researchers detected, by accurate flow-calorimetry, a *negative balance* of power and, at the same time, an excessive D_2O consumption. The calculations are performed, simply, with 4.2J/g of cooling system neglecting the (giant) value of ~2260J/g of evaporated heavy water!!
**it is possible, with a bare, virgin wire (r=25μm) immersed in water, to dissipate a power density as large as 76KW/cm^3, for several hours, without apparent damage. Experiment at: bath temperature = 20^C, I_electromigration=1.5A, R/Ro =1.33 (self heating), ΔV=1V/cm.

INVERSION OF LOADING AT LESS-MOST CATHODIC SIDE

a)**At the beginning of experiments, with new wires just assembled, the MK side of the wire has loading speed higher than LK one. Moreover, the maximum value of loading, after some hours, is larger at MK side (Fig. 3).

a')**This kind of behaviour is what expected according to: ΔV Electromigration formula, J (A/cm^2) Tafel law (the electrode "OverVoltage", then the loading, is proportional to ln of J).
b)**Some times later from the start-up of the experiment, (several hours or days, sometimes never happened), the LK side gets a loading value larger than the MK.
b')**The previous phenomenological effect is completely in disagreement with what expected and is common both with any H or D loading experiments.
c)**There is some correlation between the anomalous excess heat, under D loading, and the behaviour qualitatively shown in Fig.3: *when the LK side of the wire gets the loading larger than the MK, the excess heat always disappears.*

We realised that these kinds of unexpected results, in comparison whit the usual Coehn effect (the Electromigration formula), arise from the real situation of the wire in our experiments.
At the beginning of the experiment, according to our experimental procedure, the Pd is connected to the Ag-Cu wire (for electrical connections) by Sn-Pb solder (Fig. 5). Later on, the connection points are electrical (and, as a consequence, thermal) insulated from the electrolyte by several drops of cyanoacrylic glue. The real effect of glue isn't only for electrical insulation: it leaks some cm around the Pd wire and makes some thermal insulation, avoiding at the same time the D (or H) is taken. After the long time operation the glue can be partially dissolved in the solution, weakening the effect of "barrier". Moreover, the high pressure of H(D) has the disbinding effect on the glue and the soldering in itself: the effect is stronger at MK.
c')**The previous combined effects seem to be the key points for explanation of "reverse" electromigration effects
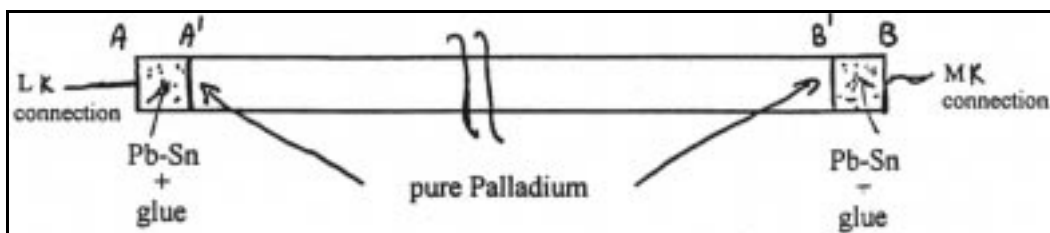

Fig. 5 – Overwiew of Pd wire at edges and central sections.

PHYSICAL EXPLANATION and CONCLUSIONS

During loading there are 2 different sections of the wire, Fig. 5:

a) **A'-B'** Area free from glue that can reach, in proper conditions, high loading and enter "γ" phase having very high diffusion speed coefficient ($>10^{-5}$ cm^2/s);

b) **A-A'** and **B-B'** where, because the combined effects of soldering and glue, the wire is in the "α" or (better) "β" phase, i.e. at the lower diffusion speed (as before quoted).

**Both sections of the wire have similar lattice constants, because the lattice increasing due to loading happens mainly during α phase nucleation.

The H(D) moves along the **A'-B'** section at high speed (10^{-5} cm^2/s) and is slowed down at **A-A'** or **B-B'** section (10^{-6}--10^{-7} cm^2/s). This condition enables large accumulation of H(D) at the border lines of **A'** or **B'** area.

As final effect:

$$\textit{the } \beta \textit{ phase promotes increasing of } \gamma \textit{ phase}$$

if, and only if, the electromigration effect is properly used, i.e. taking into account also the always effective, but uncontrollable, thermal diffusion (Fick law).

**The best results that we get in our recent experiments (99.9% J/M Pd, l=30cm, r=25μm) in a 250 μM LiOH solution in deionized H$_2$O (Vol.=2400 cm^3), were the following:

a) both wire ends bare, just connection for soldering, (A type in Fig.4), R/Ro=1.58;

b) both wire ends covered for 2.5cm with "hot covering" (C type in Fig. 4), R/Ro=1.64;

c) both wire ends covered for 2.5cm with "cold covering" (B type in Fig. 4), R/Ro<1.4.

As conclusions, we remember that, with D$_2$O, if the concentration is large enough and it is possible to promote some kinds of *fast dynamic condition*, we can get anomalous excess heat

**The pulsed operation is more successful, in respect to the DC, to "fall" into these kinds of operating conditions, but it seems less easy, for Researchers, to identify clearly (because of large electromagnetic noise emitted) each parameter for final repetition in a technological environment : both studies are necessaries.

References

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