HIGH TEMPERATURE DEUTERIUM ABSORPTION IN PALLADIUM NANO-PARTICLES

A. Marmigi[1] , A.Spallone[1], F.Celani[1], ,P.Marini[2], V.di Stefano[2]

[1]*INFN-LNF Via E. Fermi 40, 00044 Frascati, Rome, Italy*
[2]*ISCMNS (Rome group#1), Via Lero 30, 00129 Roma, Italy*

Abstract

Thin Pd wires (diameter 50 micrometers) surface oxidized through Joule heating have been loaded in a Hydrogen atmosphere at pressures in the range 1 - 10 bar. The atomic ratio H/Pd reached in the experimental conditions has been evaluated through its relationship with the electrical resistivity of Hydrogen loaded Pd. It was found that the loading rate of the surface oxidized Pd wires is exceptionally higher than with the untreated ones (full loading in a few minutes as compared with several hours). It was also observed that surface treated wires with H/Pd $\geq$ 0.75, don't lose Hydrogen even when Joule heated at temperatures up to about 150 °C in a Hydrogen atmosphere. When the wire temperature exceeds 150 °C (applied power about 12.4 W) there is an anomalous heat generation (about 3.5 W).

During an experimental test, comprising feeding the wire with stepwise increasing power values each for 500-600 seconds, followed by a period of zero power, it was observed that when the power was cut off after the period of powering with 14 W, the wire spontaneously heated for about 70 seconds releasing an estimated heat of 1650 ± 160 J, corresponding to 3940 ± 400 Kcal per mole of Pd. Peak power was $\sim$ 16 W. The wire resistance spontaneously reaches a value R/Ro = 2.40 and then slowly dropped to the original value of 1.80 at room temperature.

In a second experimental test with the same wire similar phenomena have been observed although of lower intensity but lasting over 3000 seconds. After 16 W powering for 500 seconds, the power was cut off. Again the wire heated spontaneously releasing an anomalous heat of 3600 ± 360 J, corresponding to some 13200 ± 130 Kcal per mole of Pd. The peak power was $\sim$ 3 W. The wire resistance increased spontaneously up to R/Ro = 2.01 and then slowly decreased down to 1.90.

1. Introduction

In a recent paper (J. P. Biberian [1]) it is shown that a consistent excess heat is produced when the side walls of a thin Pd tube are crossed by a D_2 flow. The heat generation only occurs if the tube has been previously oxidised in air (at 500°C).

INFN Frascati Labs (Dr. F.Celani et al.) developed, since 1990 [2], a reproducible experimental procedure for the electrochemical loading of thin Pd wires, but in 1995, also direct gas loading of Pd wires was essayed [3]. The surface oxidation of the Pd wires was just our chief technology adopted for the gas loading tests. In fact, we had found that proper surface oxidation treatments allowed for a surprisingly rapid loading rate; more surprisingly, we had observed that the wires, warmed up (by Joule heating) to ≈ 200°C, maintained unchanged their loading ratio.

The preliminary tests were obviously performed in a Hydrogen atmosphere. By adopting proper experimental conditions, we were checking whether comparable (or better) H/Pd loading ratios might be achieved *via gas*, with respect to the ones previously obtained *via electrolysis*.

Being aware that the tests were performed in H_2 (instead of in D_2) and that the obtained loading ratios were fairly poor (H/Pd ≈ 0.75), we were quite sure that no emission of excess heat could be expected. When a spontaneous warming up of the wire at "0 applied power" was recorded, we too hurriedly attributed the phenomenon to a chemical heat generation (absoption).

On the basis of the work of Jean Paul Biberian [1] our gas loading tests have been revised and are now the main object of the present paper.

Moreover, we recall results due to a fast analysis of data were presented by one of the authors (Francesco Celani) during the ICCF12 Conference, (see pg 389 of World Scientific Proceedings, ISBN: 981-256-901-4).

2. Experimental "Set-up"

Experiments have been performed employing a 30 cm long Pd wire (thickness=50μm, weight=7 mg) inserted in a steel vessel (pressure tight). In this way the heat exchange with external environment is minimized, as well as high pressure experiment can be performed.
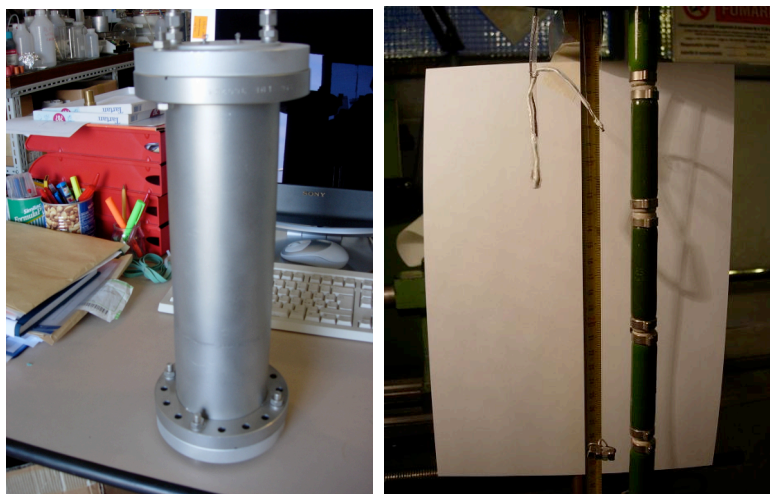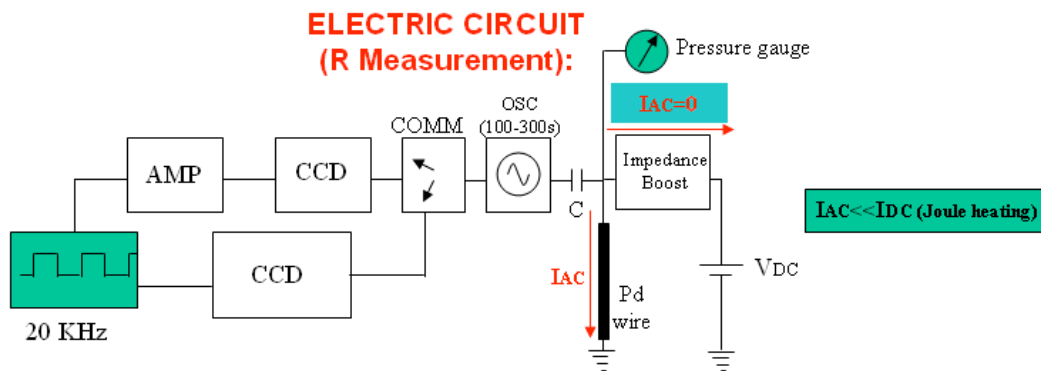

Fig. 1 Experimental set-up.

Fig. 2 Electric circuit for the measurements of Pd resistance and for Joule heating.

3. Results

The Pd wires (thickness 50μm) selected for the gas loading tests, were previously oxidised by Joule heating in air, according to the following procedure:

Basic Oxidation/Reduction cycles in air by JOULE HEATING

$$2Pd + O_2 \rightarrow 2PdO \rightarrow 2Pd + O_2$$

500÷700°C   800°C
(oxidation)   (decomposition)
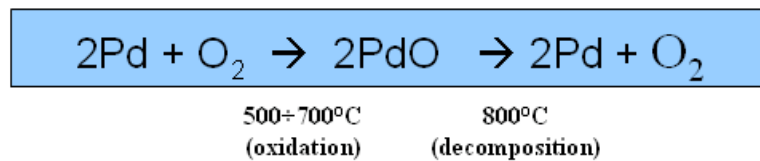
After the joule heating oxidation, the PdO layer, formed on the wire surface, was stabilised with a further heat treatment; aim of such a treatment, whose practice operations are still in progress, is to prevent (or, at least, minimise) the collapse (due to coalescence and crystallization) of the thin (and defective) Pd layer, ensuing from the H_2 reduction of the previous PdO layer.

In order to prevent coalescence, stabilizing surface treatments were effected.

$$Pd \rightarrow PdO \rightarrow \text{stabilized, defective } *Pd*$$

Stabilizing   500÷700°C
Treatments   (oxidation)

In Fig. 3.a it is shown a typical loading rate of a Pd wire in Hydrogen atmosphere (1 bar, fluxing). Thermodynamic equilibrium is reached in about 1Ms (H/Pd ratio = 0.75, at 20°C).

It is well known that such a value corresponds to the maximum of the curve $R/Ro = f(H/Pd)$, where R is the actual electrical resistance of the wire and Ro is the resistance of the virgin wire (H/Pd = 0). By comparison, in Fig. 3.b is reported the loading rate of a similar wire, oxidized in air, with no stabilizing treatment. The loading rate of the wire was improved (equilibrium reached in about 500 sec). In Fig. 3.c is shown the extremely fast loading rate for a Pd wire oxidized in air and surface-treated. Time for thermodynamic equilibrium is just 80s.

1) Blank: gas loading in H2 atmosphere, 1bar flux, without any kind of surface treatment. This test is performed in a flat cell, with gas flux (1 bar), and with a 50μm diameter Pd wire

Pd=50μm flat cell H₂ gas
p=1 bar (flowing)
D22feb06-17_38

R/R0_d
Tcelou
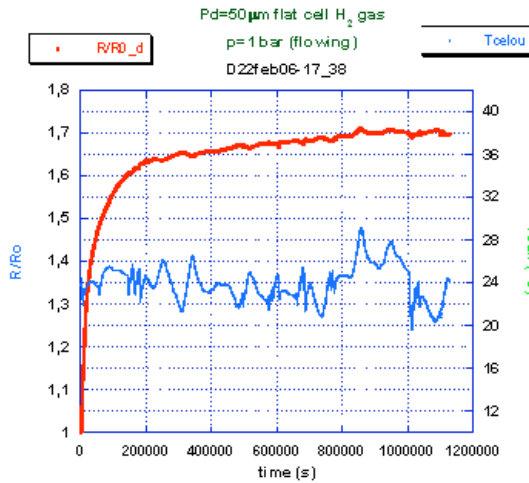
1Ms to thermodynamic equilibrium (R/Ro=1.7, H/Pd≈60%)

2) Gas loading in H2 atmosphere, 4bar, no flux, only with oxidation cycles, without surface treatment

R/R0_d

15_Nov_05_15_37
gas loading H₂, 4 bar, with surface oxidation (Joule Heating)
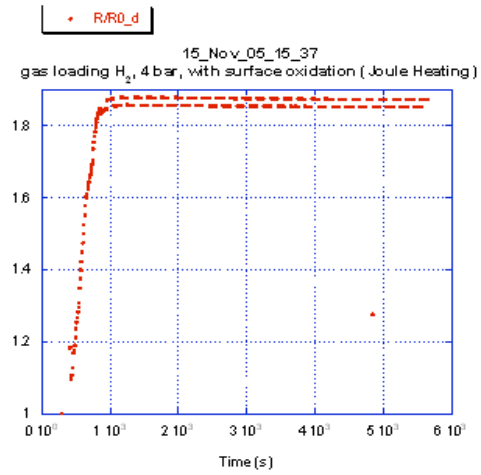
500 s to thermodynamic equilibrium (R/Ro=1.85, H/Pd≈75%)

3) Gas loading in H2 atmosphere, 3.6 bar, no flux, with surface treatments and oxidation cycles

R/R0_d

22_Dic_05-14_42
gas loading H₂ with oxidation cycles and surface treatments
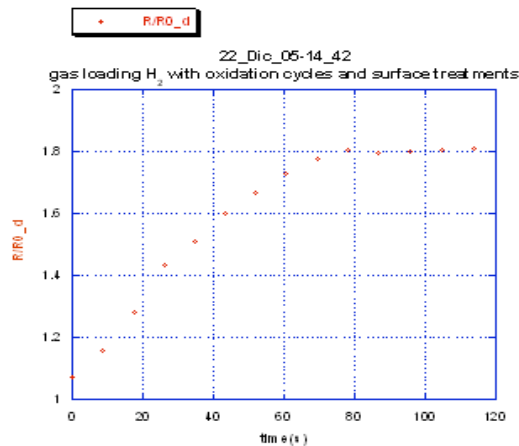
80 s to thermodynamic equilibrium (R/Ro=1.8, H/Pd≈75%)

Fig. 3 Increasing of loading rate with oxidation-stabilizing treatments.

In order to evaluate the degassing rate as a function of temperature, the wires (previously oxidised according to the above described procedure and preloaded at H/Pd = 0.75), always in contact with the H_2 atmosphere, were warmed up by Joule heating with currents of increasing intensity. The results are presented in Fig. 4.
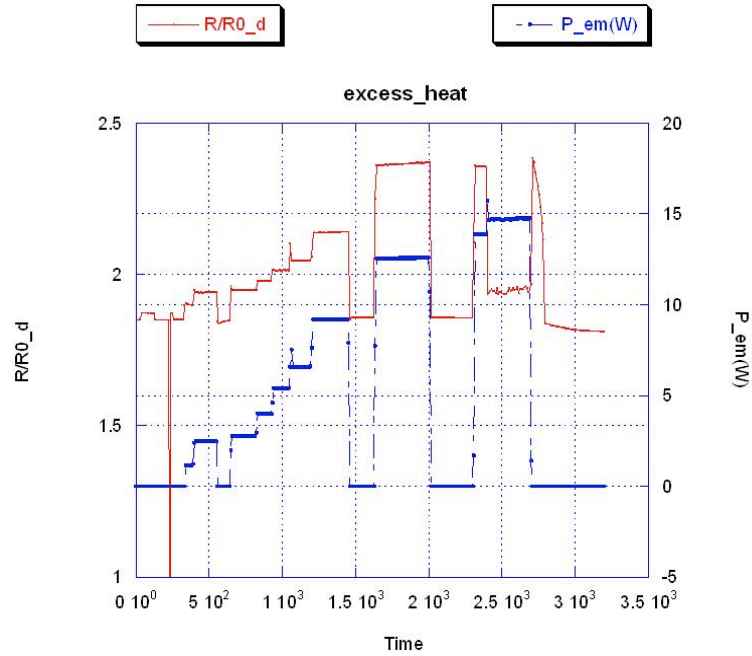

Fig. 4 The wire was warmed up with currents of increasing intensity.

In Fig. 4 the sudden change of the resistance is shown (red line) due to the applied electrical power (blue line). The starting R/Ro value of the wire (30cm long and 50μm thick) was 1.85 (H/Pd ≈ 0.75); the gas temperature was 35°C. It appears that, when the power is on, the equilibrium temperature of the wire, because of its very little thermal capacity, is reached almost instantaneously (within the 10 seconds required for the data acquirement); when the power is off the cooling down of the wire to the ambient temperature (35°C) is rapid as much.

Each test of Fig. 4 has been labelled with the progressive numbers from 1 to 12. In table 1 for each test (from 1 to 12) are reported the R/Ro values, the relative applied electrical powers and the calculated wire temperatures (°C).

Table 1

Tests	1	2	3	4	5	6	7	8	9	10	11	12
R/Ro	1.85	1.95	1.98	2.02	2.06	2.14	1.85	2.37	1.85	2.36	1.92	2.39→1.82
watt	0	2.6	3.9	5.2	6.7	9.2	0	12.4	0	13.6	14.7	0
t wire	35	67	76	89	102	128	35	201	35	?	?	?

The tests 1 → 9 will be analysed and discussed firstly; the last three, the most important ones, will be treated later, separately.

Both Fig. 4 and Table 1 show that no degassing occurs when the electric current is crossing the wire; in fact, when the power is switched off (tests 7 and 9) the R/Ro value comes back immediately to its starting value (R/Ro = 1.85).

By increasing the applied power (Fig. 3), the R/Ro values (tests 1 → 6) linearly increase, according to the relationship:

$$\frac{R}{Ro} = 0.03 \cdot W + 1.86 \tag{1}$$

The linear correlation: R/Ro = f(W) directly demonstrates that, in spite of the increase in temperature of the wire, due to the supplied power input, the loading ratio (H/Pd = 0.75) remains unchanged (i.e: no degassing occurs). In fact, let us consider the 2 following expressions, which correlate the wire temperature with the wire resistance and the applied electrical power:

$$\frac{R_t}{Ro} = Ro * \cdot \left(1 + \alpha \cdot t_w\right) \tag{2}$$

$$t_w = (W + h\, t_g)/h \tag{3}$$

Where: R_t = wire resistance at the wire temperature (t_w);
Ro = wire resistance at 20°C when H/Pd = 0 (virgin wire)
Ro* = wire resistance at 0°C when H/Pd = 0.75 (Ro* = f(H/Pd)
α = thermal resistivity coefficient (α = f(H/Pd))
t_w = actual wire temperature
W = applied power input
h = thermal exchange coefficient
t_g = gas temperature (considered constant and equal to 35°C)
By combining (2) and (3) we have:

$$\frac{R_t}{Ro} = Ro * \cdot \left[1 + \alpha \cdot \frac{\left(W + h \cdot t_G\right)}{h}\right] \tag{4}$$

The equation (4) is the explicit form of the experimentally found relationship (1). Taking into account that Ro* and α are both dependant on the H/Pd ratio, the linear dependence requires that, during the warming up of the wire, the loading ratio H/Pd (in the test 1→9) remains constant.

Established that the wire doesn't degas, it is possible to calculate with the equation (2) the wire temperatures. It is known [5] that when H/Pd = 0.75 the value of the thermal resistance coefficient is:

$$\alpha = 1.8\ 10^{-3}\ °C^{-1}$$

It is necessary first to calculate the Ro* value; as the starting temperature is 35°C, we have:

$$Ro* = 1.85/(1 + 1.8\ 10^{-3} \cdot 35) = 1.740 \tag{5}$$

by inserting the Ro* value in equation (2) it is possible to obtain the wire temperature. The calculated values are reported in Table 1.

Looking at the Fig 4, it appears that the coordinates (R/Ro versus W) of the test n° 8 are placed much above the prolongation of the straight line (1). In order to justify such a displacement, according to the equation (1), the applied power would have been 16.7 Watt, instead of 12.4 Watt actually supplied; that is: 4.3 Watt in excess. It should be noted that such an excess power, because of the very little mass of the wire ($\approx$ 7 mg), is really relevant: 0.61kW/g!
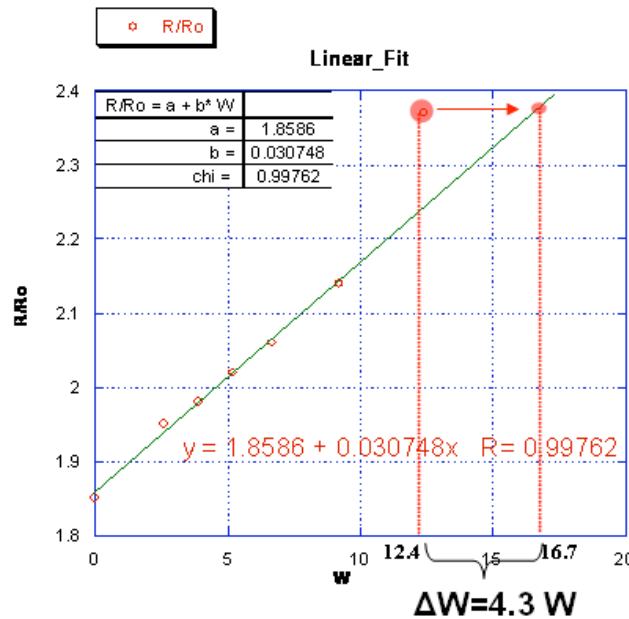

Fig. 5 First evidence of excess heat.

It also appears that the observed excess heat requires a triggering temperature; its value should be located in between 128°C (test n° 6; 9.2 Watt) and 152°C, which is the temperature corresponding to the power of 12.4 Watt, if no excess heat had been produced.

Obviously, the test n° 8, alone, may be considered at the most an interesting and encouraging cue for additional tests. It shouldn't worthy of mention in a scientific paper if a surprisingly effect, capable to confirm the reality of the excess heat produced in the n° 8 test, was not occurred.

Test N=12 shows that when power is switched off R/Ro grows up to 2.4. We know that the only reason of R/Ro growing above 1.8 is the wire is warming up (Ro is not corrected with temperature).

The R/Ro of the wire stays over 1.8 for about 100 seconds, before returning to 1.8. The integral of excess power yield is about 1 kJoule that means 4 MCal per gram-atom of Pd. So, it is not compatible with any known chemical heat.
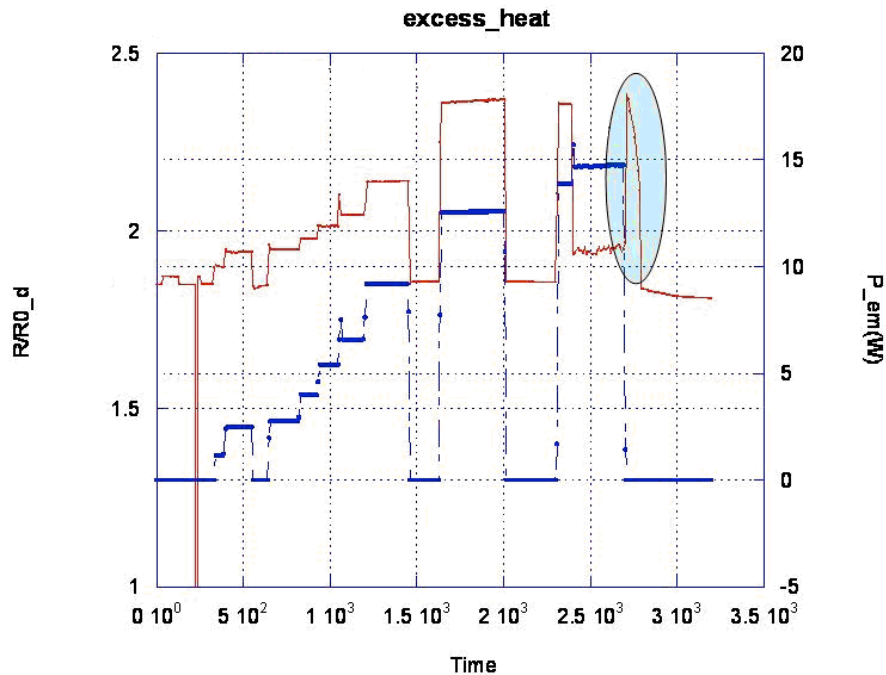
Fig. 6 Evidence of excess heat at W=0

4. Conclusions

Gas loading of thin Pd wire has been studied:
 a) Blank loading→1Ms to thermodynamic equilibrium;
 b) After surface oxidation→500s to thermodynamic equilibrium;
 c) After surface stabilising treatment→80 s to thermodynamic equilibrium.

Excess heat was found in a loading gas experiment:
 a) No degassing demonstration;
 b) Excess power of 4W was found when power applied was 12.4W;
 c) Excess heat of 4MCal/mol was found when power applied was 0W;
 d) Experiment was reproduced.

References
[1] J.P. Biberian and N. Armanet "Excess heat production during D2 diffusion through palladium", ICCF13, June 25-July 2, 2007, Sochi (Russia), printing by World Scientific.
[2] F. Celani, A. Spallone, S. Pace, L. Liberatori, A. Saggese, V.Di Stefano, P. Marini. "Further Measurements on Electrolytic Cold Fusion with D2O and Pd at Gran Sasso Laboratory." Fusion Technology, vol. 17, no. 4 pg. 718-724 (1990).
[3] P. Marini, A. Spallone and P. Tripodi. " Superconduttività a temperatura ambiente?" XXI Secolo Scienza e Tecnologia, Anno VII n. 2, Apr.-Giu. 1996, pg. 41-45.
[4] B. Baranowski and R. Wisniewski, Phys. Stat. Sol., 35 (1969), p. 539.
[5] J.C. Barton, F.A. Lewis and I. Woodward (1963), Trans. Faraday Soc. 59, 1201.