

**Towards a high temperature CMNS reactor:  
nano-coated Pd wires with D<sub>2</sub> at high pressures.  
Identification of main control parameters,  
development of simple tests about quality of coating.**

*New: possible evidence for Planck black-body law “violation”??*

**Francesco Celani**<sup>(1)</sup>, P. Marini<sup>(2)</sup>, V. di Stefano<sup>(2)</sup>, M. Nakamura<sup>(2)</sup>,  
O. M. Calamai<sup>(1)</sup>, A. Spallone<sup>(1)</sup>, E. Purchi<sup>(2)</sup>, V. Andreassi<sup>(1)</sup>, B. Ortenzi<sup>(1)</sup>,  
E. Righi<sup>(1)</sup>, G. Trenta<sup>(1)</sup>, G. Cappuccio<sup>(1)</sup>, D. Hampai<sup>(1)</sup>, F. Piastra<sup>(1)</sup>, A. Nuvoli<sup>(1)</sup>.

- 1) Istituto Nazionale di Fisica Nucleare, Laboratori Nazionali di Frascati, Via E. Fermi 40, 00044 Frascati (Rome)-Italy.
- 2) International Society of Condensed Matter Nuclear Science, Rome#1 ISCMNS\_Group Via Lero 30, 00129 Rome-Italy.

***Collaboration with:***

\* **U. Mastromatteo.** STMicroelectronics, Via Tolomeo1, 20010 Cornaredo (Mi).

\* **A. Mancini.** ORIM SpA, Via Concordia 65, 62100 Macerata

\* **F. Falcioni, M. Marchesini, P. Di Biagio, U. Martini.** Centro Sviluppo Materiali,  
Via di Castel Romano 100, 00129 Roma, Italy

\* **L. Gamberale, D. Garbelli.** Pirelli Labs, Viale Sarca 222, 20126 Milano-Italy

*The work was partially supported by **Lam.Ba. SrL Caluso (Turin) Italy.***

## OUTLINE

- 1) Improved measurements on “Washington type” reactor ( $P < 10$  bar; max wires temp.  $500^{\circ}\text{C}$ ; reactor SS wall temperature  $< 40^{\circ}\text{C}$ ): **main results of ICCF14 confirmed (i.e. anomalous excess power, stable over time, up to  $400\text{W/g Pd}$ ).**
- 2) \*\*\* Experiments on **HP (60 bar)-HT ( $600^{\circ}\text{C}$ ) reactor wall** are still in **progress**: experienced *heavy problems* coming out because degassing impurities (specially **S, P**) from **SS** (304, 316) used in the reactor wall. The scavenger effect of  $\text{H}_2$  (and  $\text{D}_2$ ) on SS makes the impurities problem quite difficult to be overcome. For such reasons we designed and build a new, **multilayer (SS/Cu 3N)**, reactor that is now under the stage of final test.

- 3) Studied, in same details, the experimental effect of **GIANT REDUCTION** of Pd wire length due H<sub>2</sub> (or D<sub>2</sub>) to loading → deloading cycles. Consequences about anomalous excess heat generation, detection and long time stability. **Live video of the effect** (by digital video camera) and **correlation with data acquired by on line computer** (1 complete set of data every 1 second).
- 4) **NEW EFFECT** (found after ICCF15 abstract submission): evidences for **possible Planck-Stefan-Boltzmann black-body law ( $M = \sigma * T^4$ ) “violation”** due to nanostructures also in our experimental set-up. **Such “violation” predicted by Max Planck himself.** Only very recently (July 2009) experimentally confirmed (at MIT) but in very local situations and specific materials.

## Description of (1)

Verification, and instrumental improvements, of measurements presented at ICCF14 on anomalous excess heat using thin ( $\Phi=50\mu\text{m}$ ) and long ( $l=65\text{cm}$ ) Pd wires with **surface covered by several nano-materials** (nominal  $\Phi=9\text{nm}$ ,  $S=300\text{m}^2/\text{g}$ ) Pd included. **The excess heat is at macroscopic levels (up to 5W), high temperatures (400-500°C), the power density was as large as 400W/g of Pd.**

*\*\* We decided to modify further our previous preparation procedure (very shortly described also at ICCF14) of nanocoating proper (several) materials onto the Pd wire surface in order to make the **nanocoated wire more “resistant” to aging effects due to several loading-unloading cycles.***

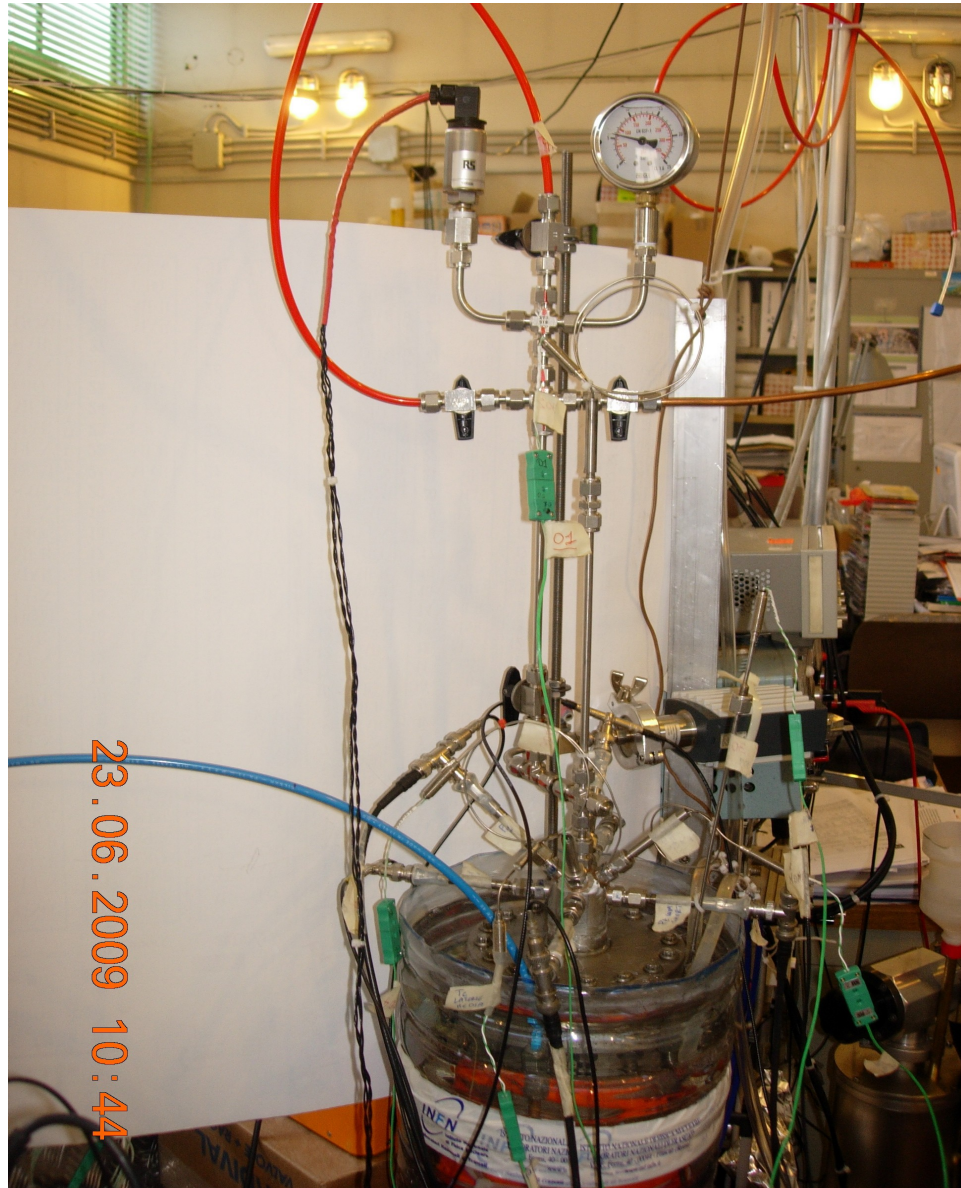
*\* In addition, the material of the **braid** was **changed from glassy fibre to***

**quartz** (in order to “work” from about **520°C** up to **850°C**): such changing, in principle, improves the thermal coupling between braids (thermal conductivity of quartz is higher than glass) but increases at the same time the thermal losses (wire temperatures lower at the same input power).

The main instrumental improvement was the *addition of another long Pt thermometer* **surrounding** all the previous 3-wires braid. The length of such Pt thermometer is 190 cm, i.e. about 3 times longer in respect to the (Pd-Pt-Pt) wires inserted into the braid. Moreover: were added other 2 thermocouples inside the pressurized SS chamber; the outside cooling water’s temperature was made homogeneous by bubbling air. The data acquired, after correction by calibrations using  $^4\text{He}$ , were consistent each-other.







23.06.2009 10:44

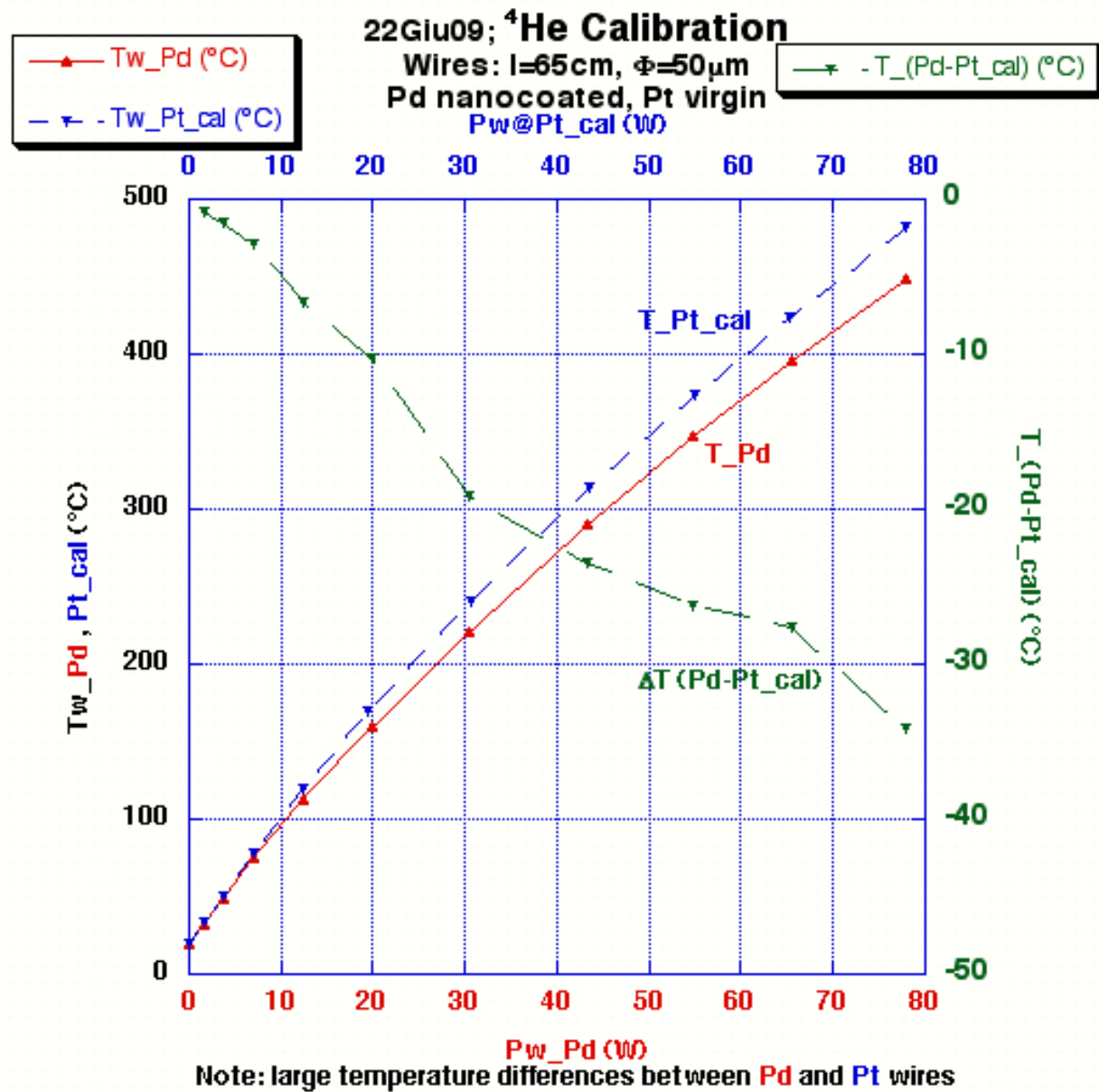


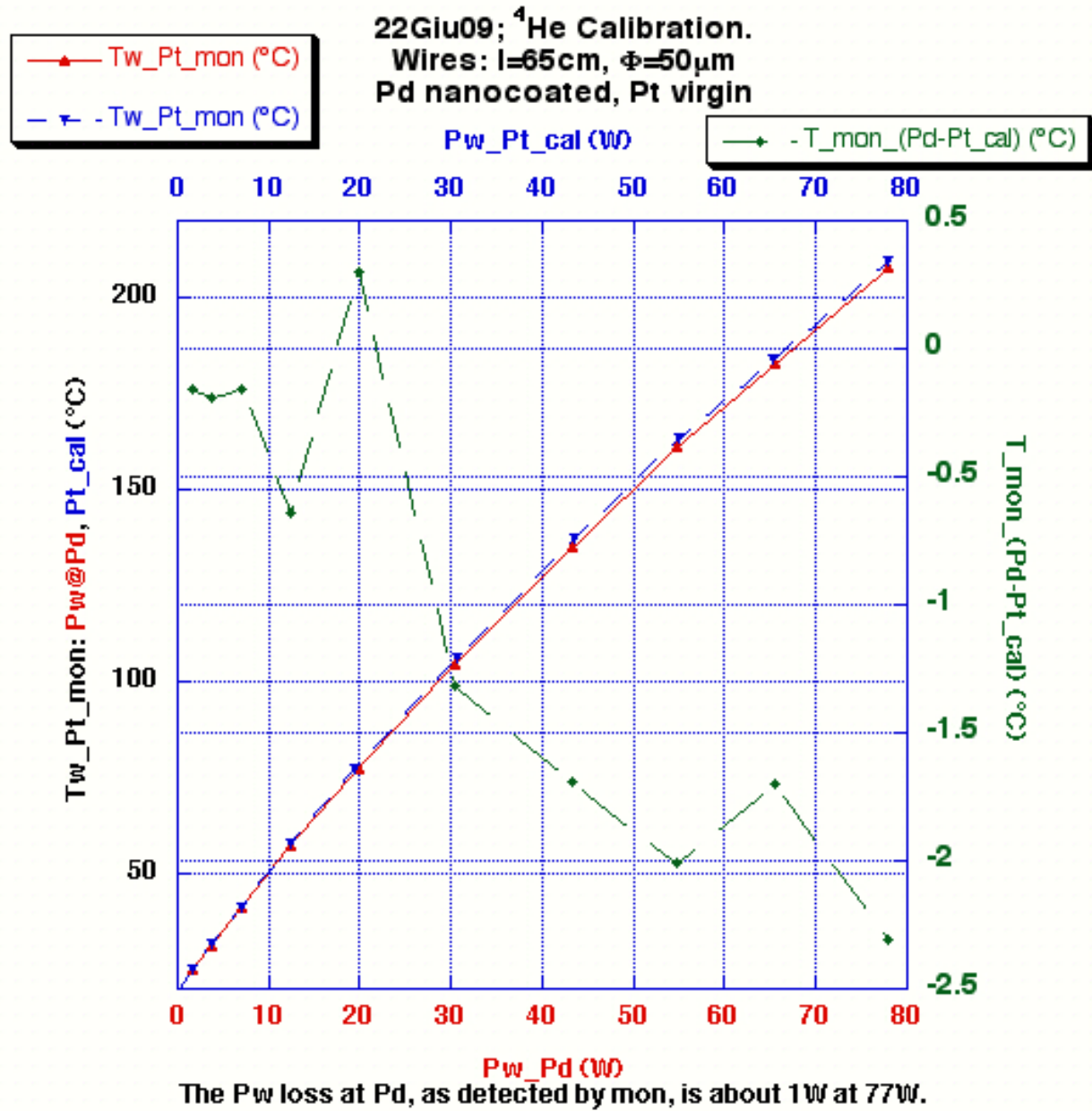
**\*\* According to our measurement procedures, were made experiments in  $^4\text{He}$  (calibrations) and subsequently  $\text{D}_2$  gas atmospheres (both at 6.5bar). Moreover, were made new experiments also with a *mixture of  $\text{D}_2$  ( $P=4.62\text{bar}$ ) and Ar ( $P=1,68\text{bar}$ )*. The rational was to study if the effect of larger temperature (the thermal conductivity of Ar is over 7 times lower in respect to  $\text{D}_2$  at temperature between 35 and  $90^\circ\text{C}$ ) of Pd wire (at constant power) could compensate for lower pressure of  $\text{D}_2$  (i.e. from 6.5 to down 4.6 bar) or even improve the over-all amount of anomalous excess heat production. About gas thermal conductivity, adding 24% of Ar to pure  $\text{D}_2$ , it is reduced (at  $95^\circ\text{C}$ ) of 56% (from 151 to 96  $\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ).**

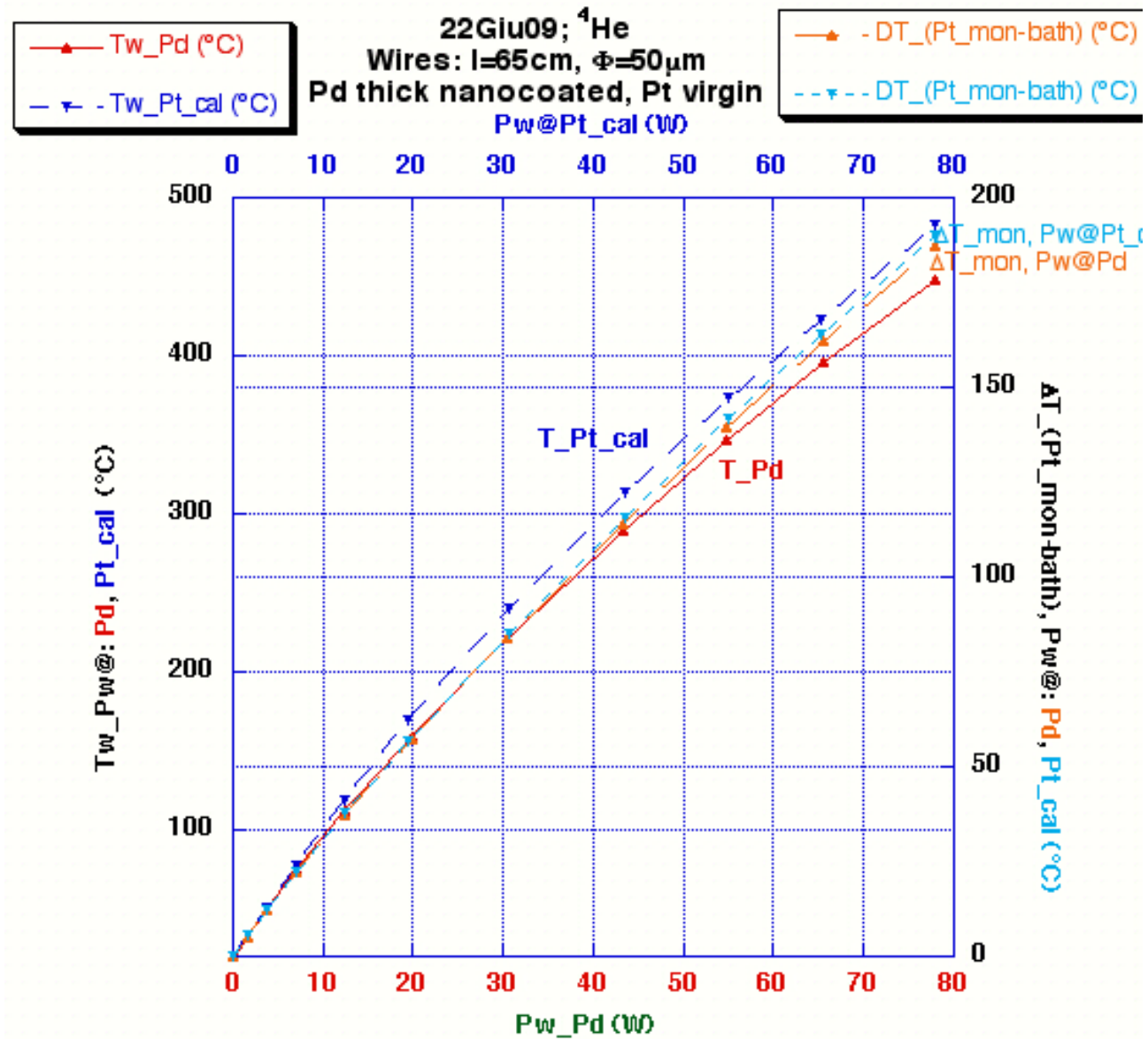
***The answer was that the increase of temperature improved, in a large way, the anomalous heat production and overcame the deleterious effect of  $\text{D}_2$  partial pressure reduction.***

## Key characteristics of nanocoated Pd wires

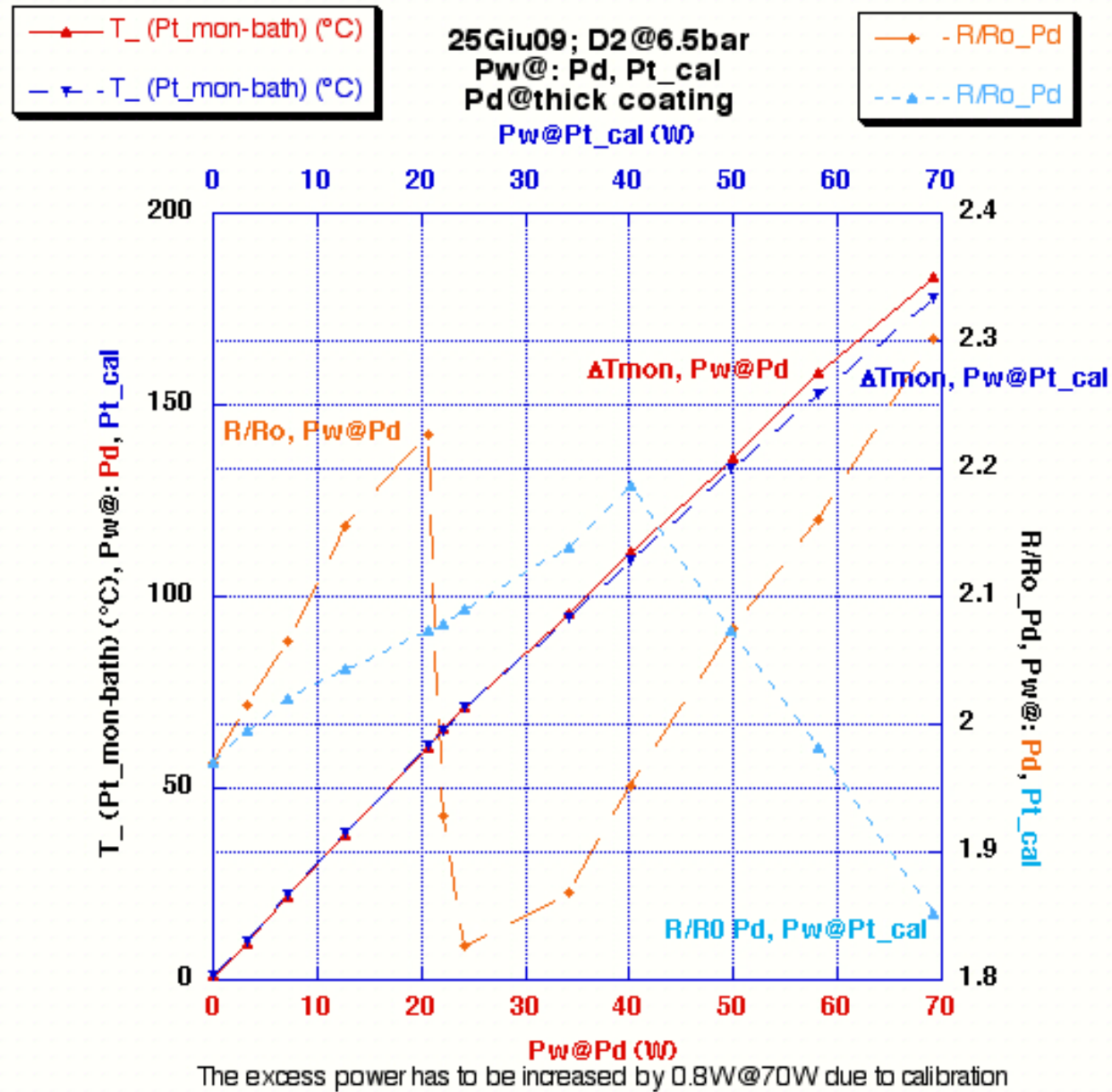
- 1) The loading time, using a pressure of Hydrogen or Deuterium gas of about 6.5bar, is of the order of 10-20 seconds.
- 2) The deloading time, using vacuum, is quite long and depends on the “quality” of nanomaterials deposited on the Pd surface: **as a general behaviour, as short was the loading time as long, and difficult, will be the deloading procedure.** Several times it was necessary to reach, under vacuum, by Joule heating, temperature as high as 350-400°C for time as long as 1-2 hours, to get a “full” deloading.
- 3) The effect, observed since 2002 even in electrolytic experiments, was called by us the **DIODE EFFECT**. In other words, the good wires adsorb very easily the H<sub>2</sub> (or D<sub>2</sub>) and are very difficult to desorb them.

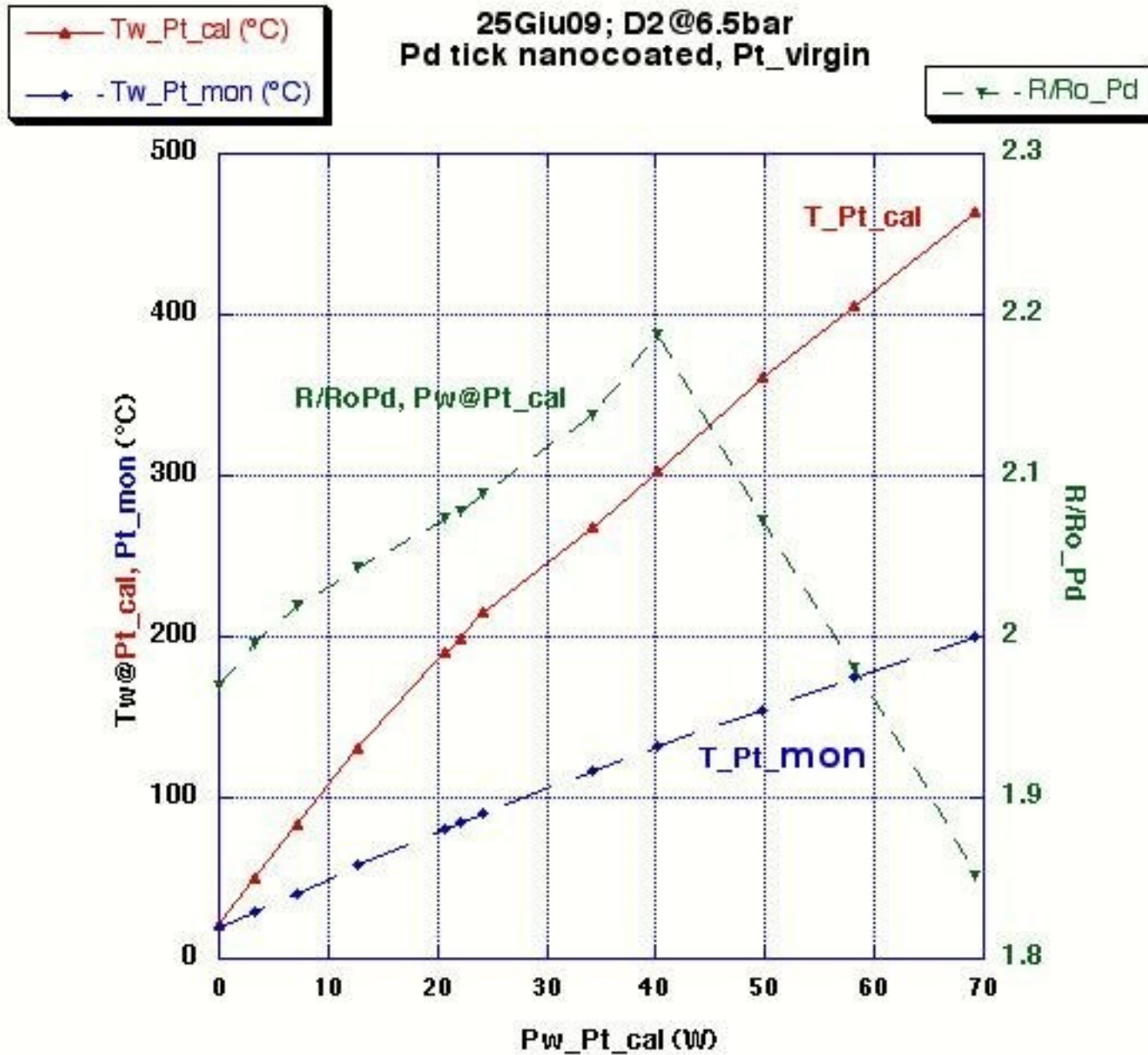




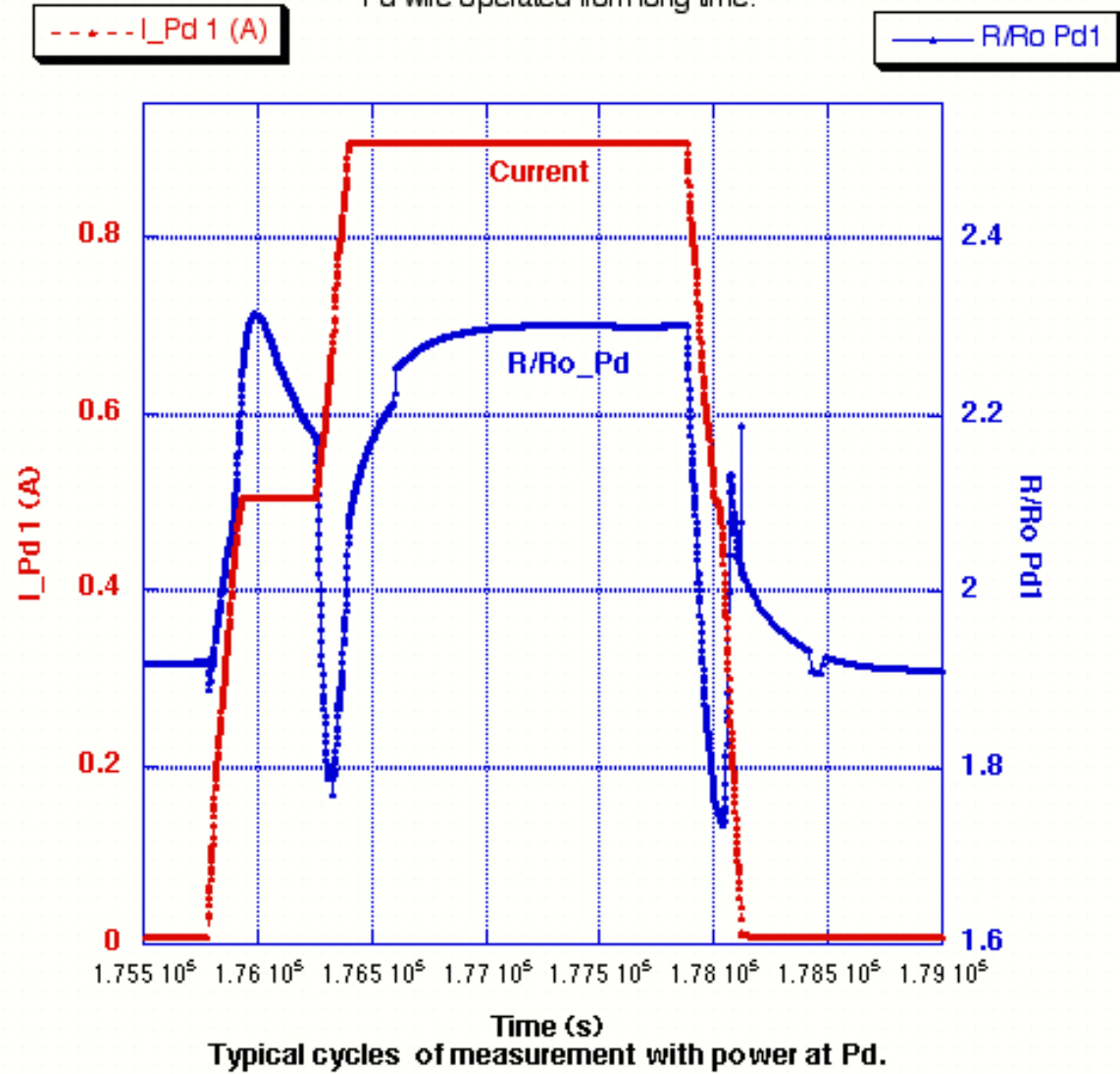


*Temp. detected by Pt\_mon is lower whit  $P_w@Pd$ . Power lost  $>1W@75W$*

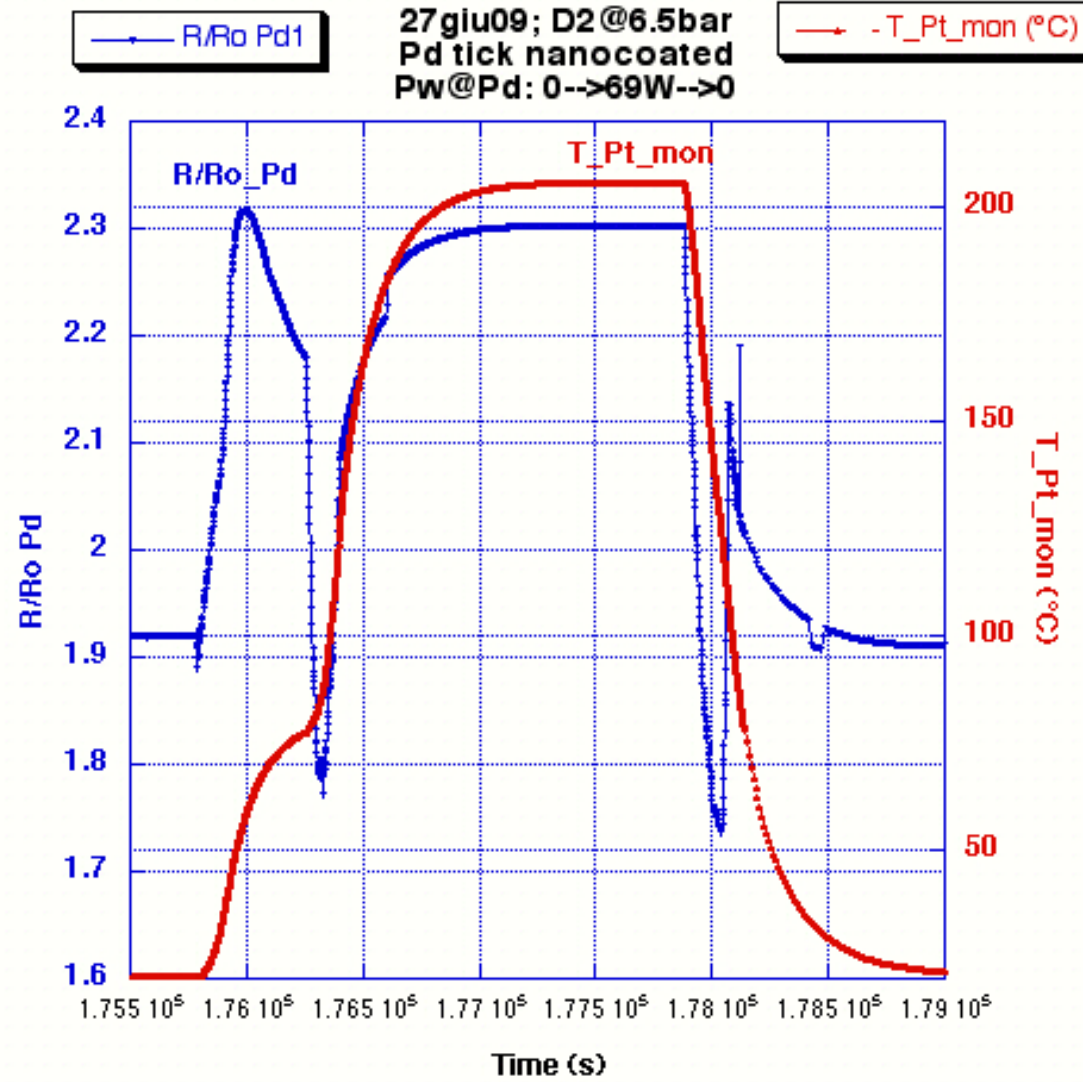


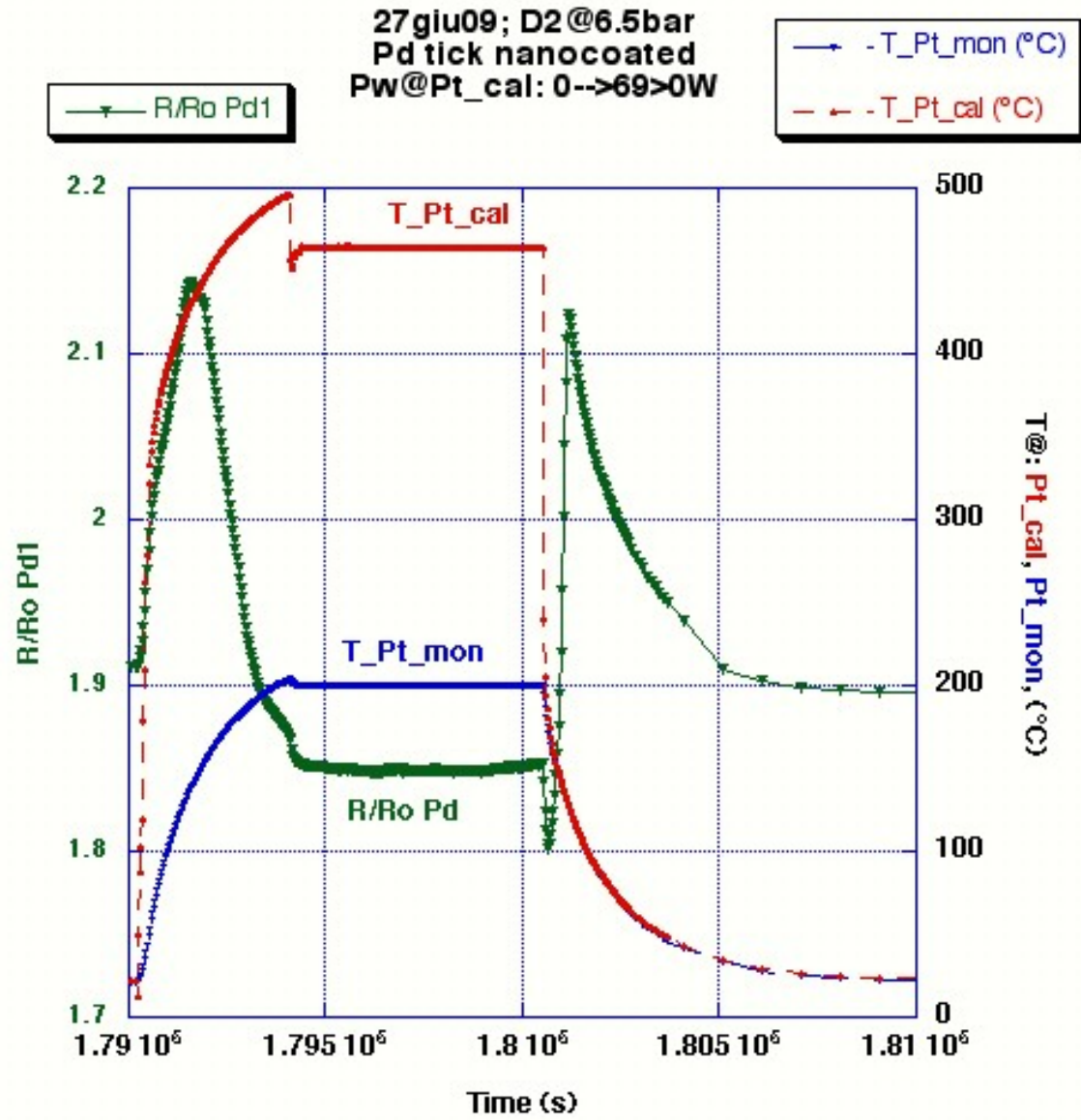


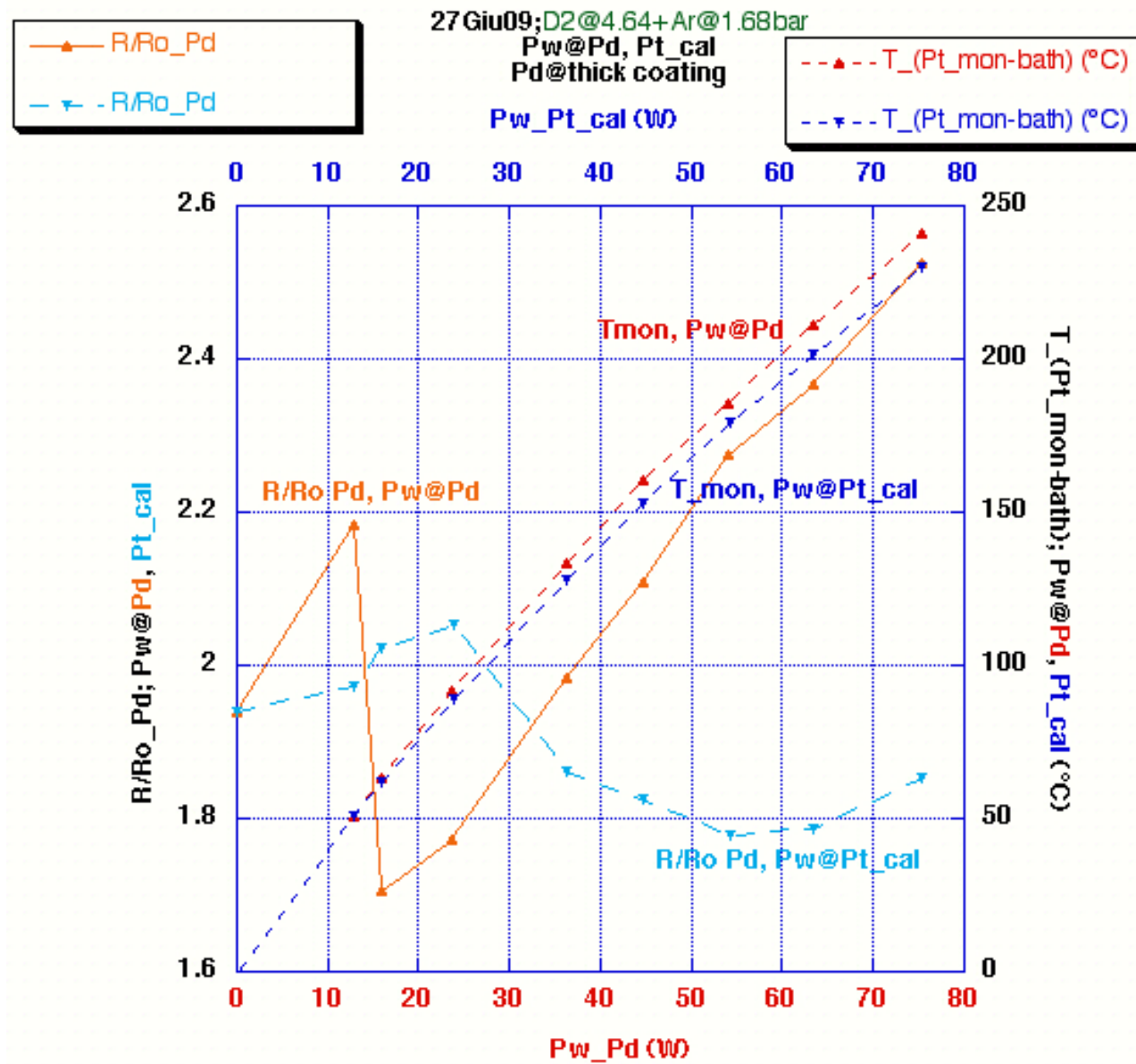
27giu09. D2@6.5bar  
Pd tick nanocoated  
Pd wire operated from long time.





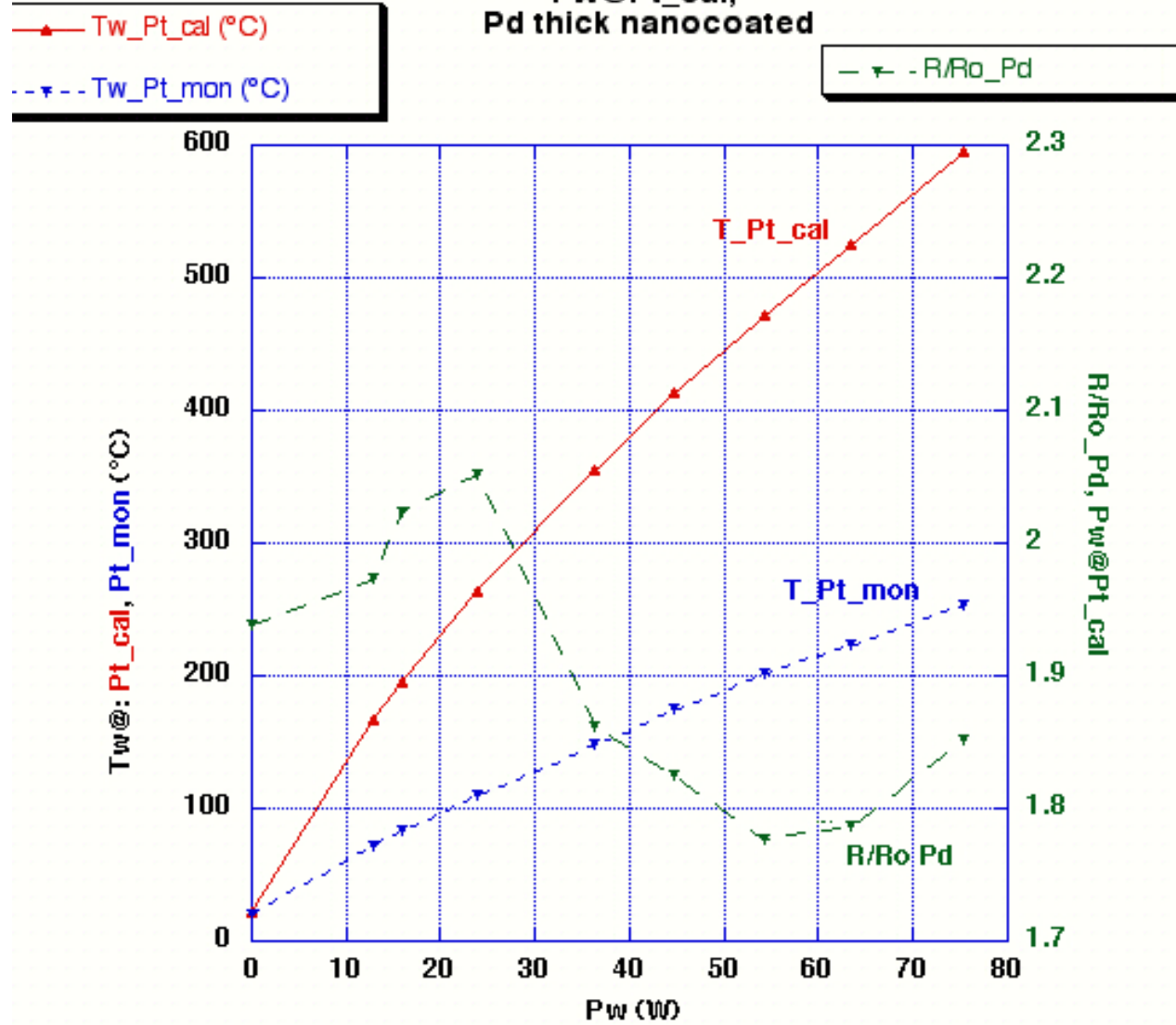






In respect to pure D2 gas, are larger wire temperature and gain.

27Giu09; D2@4.64+Ar@1.68bar  
 Pw@Pt\_cal,  
 Pd thick nanocoated



With Ar+D<sub>2</sub> mixtures the wires temperatures, at same power, are larger.

## Description of (2)

Studies about **giant reduction** of Pd length due to loading-> deloading cycles ( $H_2$ ,  $D_2$ ). Experimentally, obtained (in few hours) a Pd resistance reduction of **over 500%** from the initial value.

***New discovery:*** the wires that are ***weakly affected*** by such phenomena produced measurable excess heat: ***nanocoating is effective to get it.***

Made, very recently, a systematic work on correlation between the geometrical reduction of wire length (*visual observation* through a transparent tick glass pressurised cell) and resistance reduction. Found very clear correlation between the 2 regimes induced by strong energy pulses to the wire: initial fast (few seconds) H<sub>2</sub> deloading (and related length reduction) with following usually slow (from 5 up to hundreds of seconds) reloading with correlated *partial* re-increasing of length.

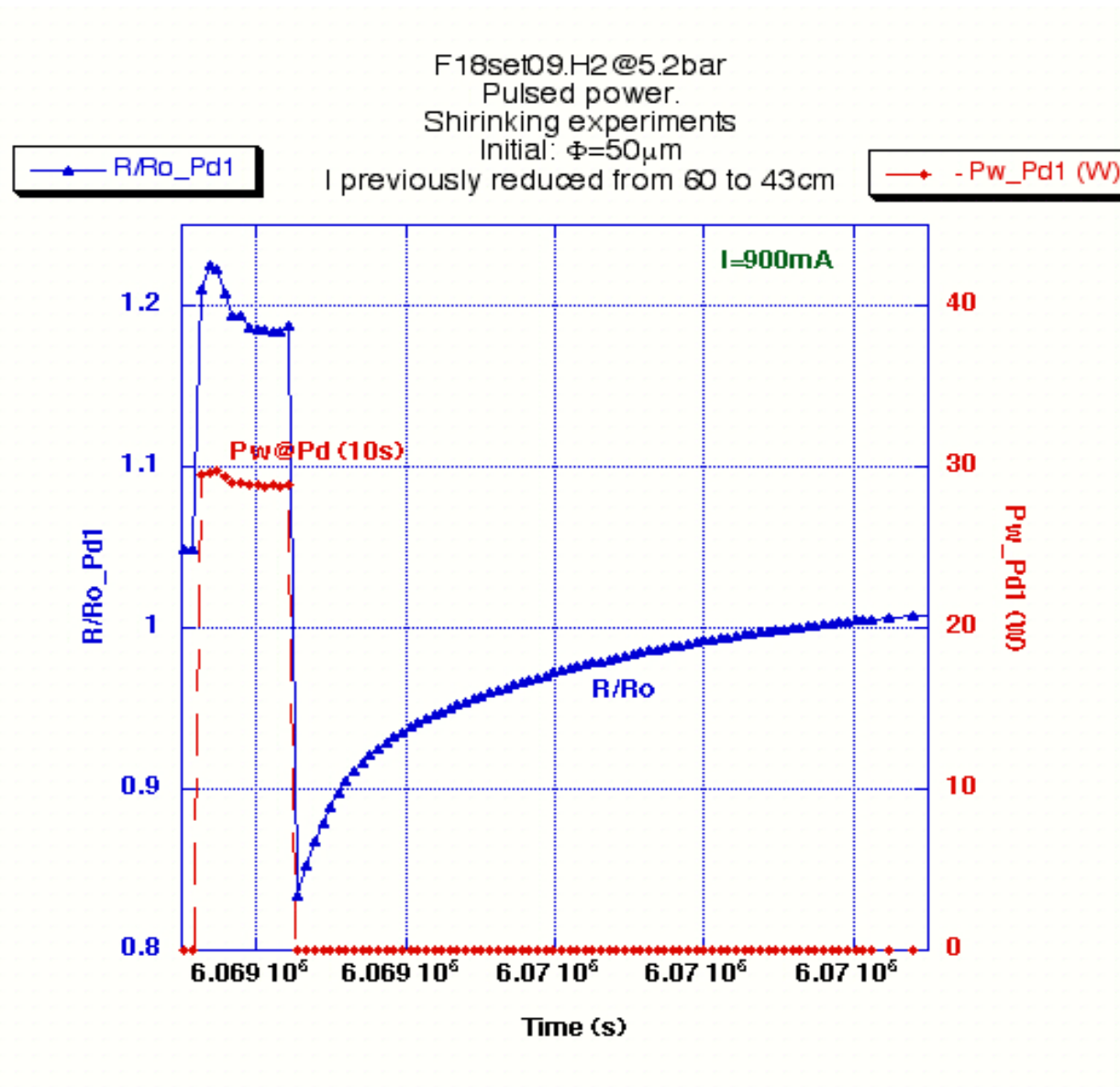
*Key point: the speed of reloading (H<sub>2</sub> or D<sub>2</sub>) depends markedly on the conditions of Pd surface: we measured from times as short as less than 5 up to thousands seconds. In respect to only oxidized Pd wires, nano-coated wires have systematically lower values of reloading time.*



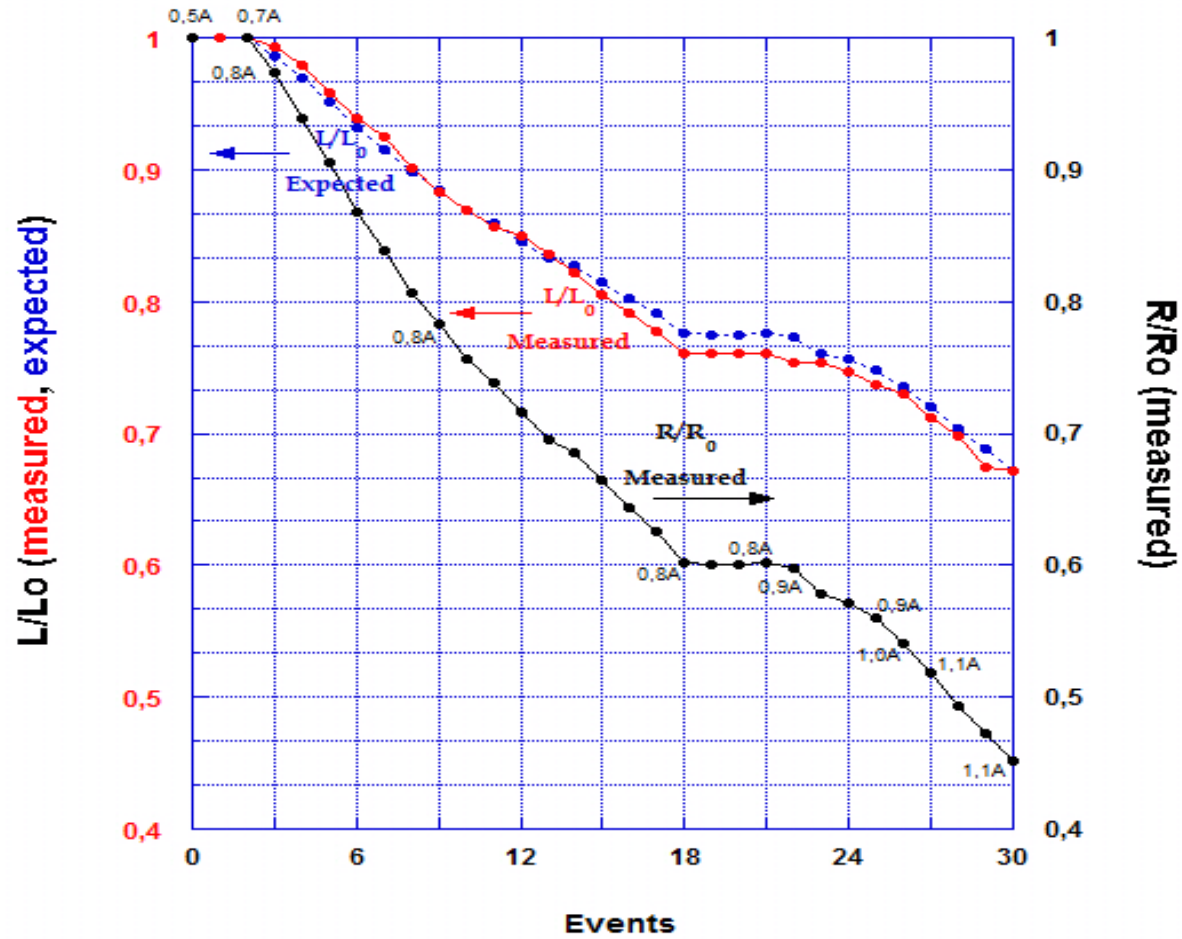




**Live movies of Pd wire shrinking under  
electrical power excitation**



Expected shrinks:  
 $r = \text{const.}$   $V = L \cdot S = \text{const.}$   $R = r \cdot L / S$   
 $L/L_0 = (R/R_0)^{1/2}$



## Description of (3)

Analysed, in deep, the effect (by us discovered since 2008 and presented shortly also at ICCF14) that the Pd wires **surfaces** (properly **nano-treated**) have **temperatures lower** than expected in comparison with a similar Pt wire under the same power of Joule heating (calibration by  $^4\text{He}$  gas and first region of “excess power” using  $\text{D}_2$ ). Developed a new apparatus (thick transparent glass) to study, in deep, such effect: indications that were found macroscopic **apparent violations** of “black-body” radiation law (Planck and following Stefan-Boltzmann). **Max Planck** himself recognized that the law bearing his name

***is not valid when the characteristic length scales are comparable to the wavelength of thermal radiation.***

Such **apparent violation** was experimentally proved, for the first time, in a very sophisticated experiment performed at MIT (S. Shen et al.; Nano Letters, 2909-2913, 2009) using SiO<sub>2</sub> microsphere and a flat surface at distances down to 30nm separation in vacuum. Almost no results are allowable for macroscopic systems. *The nano-structures we developed seem to play an important role to explain our ICCF14-5 results and are stable enough (versus temperature, up to 500°C) to can be used even for practical applications (improved heat dissipation in vacuum, e.g. electronics used for satellites).*

**Planck (Stefan-Boltzmann) law:**

$$\left(\frac{2\pi^5 \cdot k_B^4}{15h^3 \cdot c_0^2}\right) \cdot (T^4 - T_a^4) = 5.672 \cdot 10^{-8} \cdot (T^4 - T_a^4) \quad [W \cdot m^{-2} \cdot K^{-4}]$$

$k_B$ =Boltzmann const.  $1.38 \cdot 10^{-23}$  [J/K];  $h$ = Planck const.  $6.261 \cdot 10^{-34}$  [J\*s];

$c_0$ =speed of light in vacuum  $2.99792458 \cdot 10^8$  [m/s];  $T$ =Temperature [K]

## Procedure of experiment (3)

The procedure to make experiments is quite simple in principles but long in operation times.

### Type Ox experiment.

- a) Measure the heat losses of the wire, in vacuum, changing the input power. In the first experiment the Pd wire was previously well degassed under vacuum at high temperatures (up to 850°C) and stress released (with concomitant lattice reconstruction and grain growing) for enough long time (30-60m).
- b) Later, the same wire is oxidized in open-air atmosphere, without opening the reactor, for about 60m at 650°C.

- c) Make vacuum again to the same value of previous measurement (usually  $10^{-4}$  bar).
- d) Measure the heat loss as point 1) and note the differences, if any. The difference can be due to oxidized layers (with nano-micrometric dimensions) of Pd surface.
- e) After the cycle d) was ended measure again the heat loss and compare the results with point a). If all went well the results of a) and e) as to be very similar.

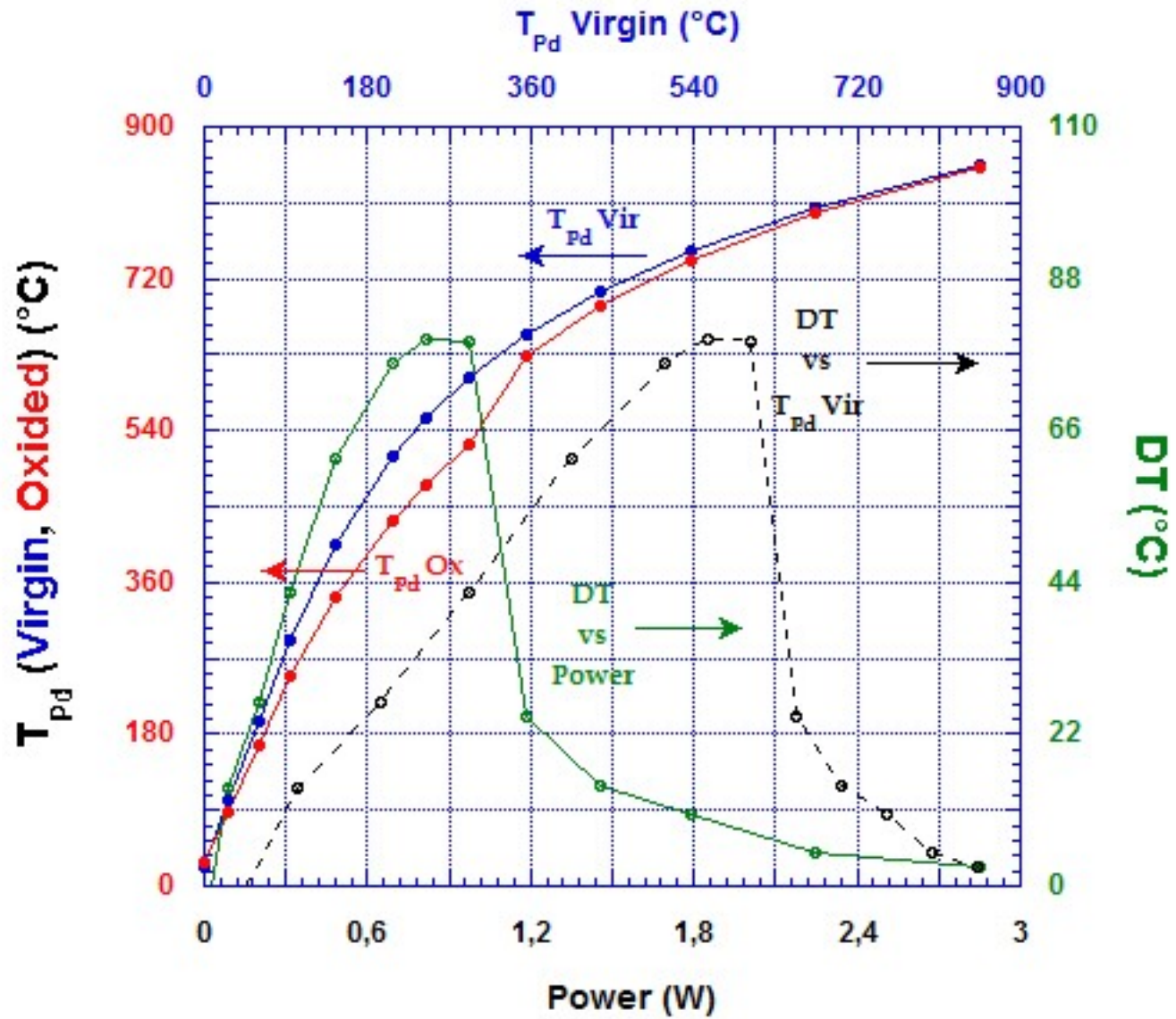
## Type Ox $\rightarrow$ H<sub>2</sub> $\rightarrow$ mild temperature degassing experiment.

- f) Same procedure of a) and b).
- g) Add H<sub>2</sub> (at 5 bar) and observe loading. If enough fast (<20 seconds) to reach  $R/R_o=1.8$  the procedure of oxidation was correct.
- h) Evacuate the chamber and make vacuum. Then, at temperatures not over 350°C deload the wire until the  $R/R_o$  ratio will be constant. At this time take off the power and measure again, at room temperature, the  $R/R_o$  value. If all went well the  $R/R_o$  value has to be decreased to about 0.96.
- i) Make cycles of  $P_w \rightarrow$  Temperature, like d). The difference in the behaviour can be due to changing of surface, with larger values of it, due to loading-deloding H<sub>2</sub> cycle.

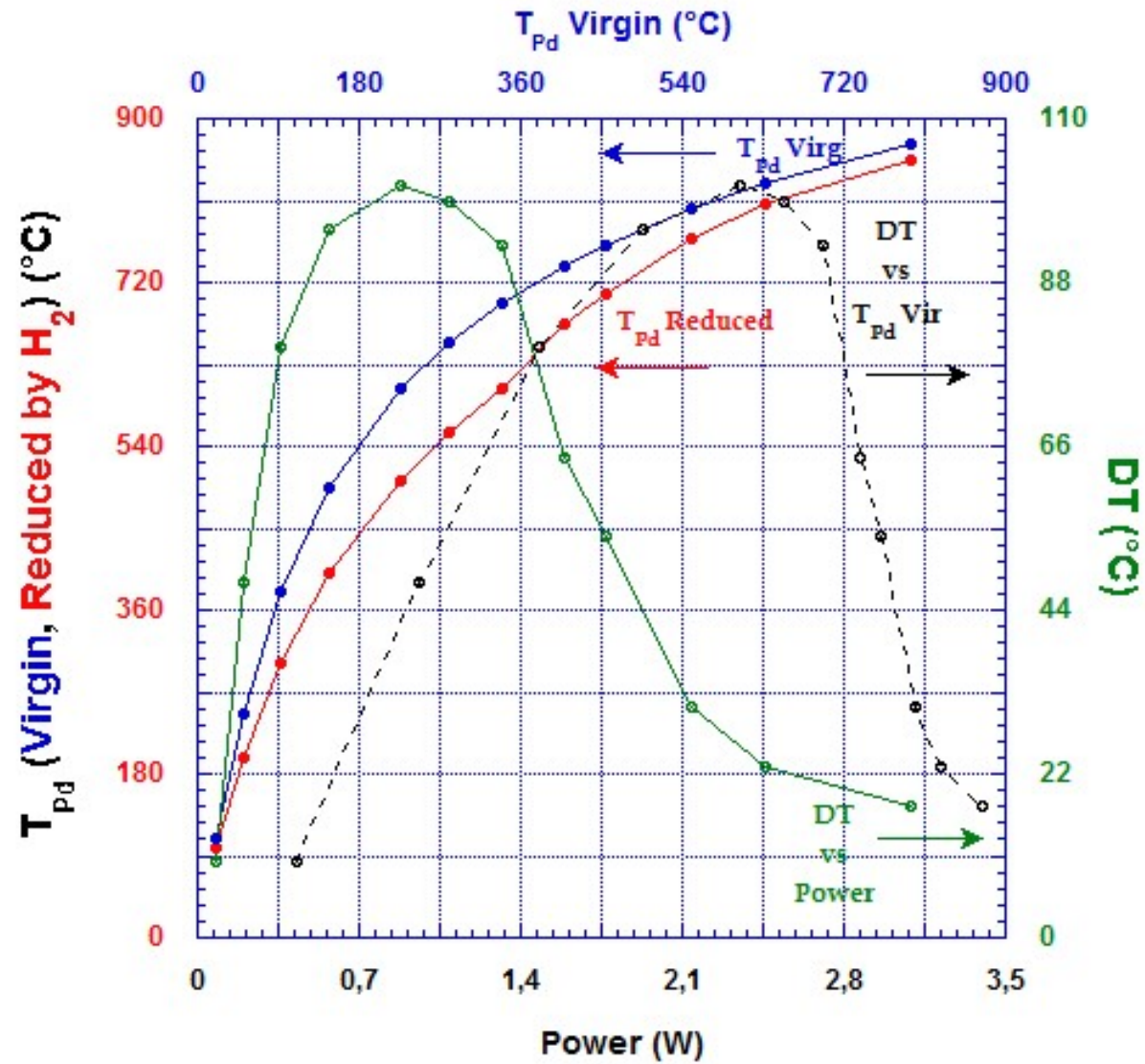


j) Evaluate if the differences are significant enough to be ascribed to some (new) effect not compatible with the expected changing of surface area and, overall, if the peak of the temperature of surface decomposition are significantly different from cycles of “pure” oxidation.

Pd wire,  $l=600$  mm,  $\Phi=50$   $\mu\text{m}$ , U shaped [15 Sep 09]



Pd wire,  $l=592$  mm,  $\Phi=50$   $\mu\text{m}$ , U shaped [18 Sep 2009]



## Conclusions

According to the experimental results we can argue that:

- 1) The **data** presented at **ICCF14** were **reconfirmed**;
- 2) There are indications that **increasing** the **temperature** (e.g. the experiment with pure D<sub>2</sub> against the mixing D<sub>2</sub>+Ar) and (?) **pressure** on nanocoated Pd wires can be possible to **increase** the overall **efficiency**. We hope that our improved (multi-layer: SS&Cu 3N) high temperature, high pressure reactor, at present in the final stage of construction, will allow to overcome the problem of “poisons” coming out from the reactor wall (at least, we identified the **S**, at 300-700 ppm concentration, that is present in the typical SS AISI 304 and 316 used for pressurized vessel).

- 3) The specific nanocoating (of thin and long Pd wires) improved the overall stability of Pd wires against **“aging” effects** due to several loading-deloding cycles (i.e. the length of wire is weakly affected by such effect).
  
- 4) The well know, deleterious, effect of decreasing the amount of excess heat production after the “first” cycle seems not to be present in our experimental materials, set-up and operating conditions. *We can imagine that the continuous flowing of “fresh” Deuterium inside and through the Pd surface “clean up” the ashes (<sup>4</sup>He according to **Yoshiaki Arata** and other Scientists) of CMNS reactions.*

5) There are indications that the **surface modifications** “induced” by Pd oxidations, H<sub>2</sub> absorption and nanocoating (about the last one the experiment now is in progress), can be used even in applications (like *enhanced heat dissipation in vacuum*) very far from the traditional one of CMNS studies: such effect can be used at temperature as large as 500°C. ***In other words, another new effect that was found, by serendipity, just because (in deep) CMNS studies.***