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**HIGH TEMPERATURE DEUTERIUM ABSORPTION IN PALLADIUM
NANO-PARTICLES**

V. Andreassi¹⁾, G. Cappuccio¹⁾, F. Celani^{1)*}, P. Di Biagio⁵⁾, V. Di Stefano²⁾, F. Falcioni⁵⁾,
F. Fontana⁷⁾, L. Gamberale⁷⁾, D. Garbelli⁷⁾, D. Hampai¹⁾, M. Marchesini⁵⁾, P. Marini²⁾,
A. Marmigi¹⁾, A. Mancini³⁾, U. Mastromatteo⁴⁾, M. Nakamura²⁾, E. Purchi²⁾,
P. Quercia¹⁾, E. Righi¹⁾, P.G. Sona⁶⁾, A. Spallone¹⁾, F. Todarello²⁾, G. Trenta¹⁾

¹⁾ INFN-LNF Via E. Fermi 40, 00044 Frascati, Rome, Italy

²⁾ EURESYS, Via Lero 30, 00129 Rome, Italy

³⁾ ORIM SpA, Via Concordia 65, 62100 Piediripa, Macerata, Italy

⁴⁾ STMicroelectronics SpA, Via Tolomeo 1, 20010 Cornaredo, Milan, Italy

⁵⁾ CSM SpA, Via di Castel Romano 100, 00129 Rome, Italy

⁶⁾ Via S. Carlo 12, 20090 Segrate, Milan, Italy

⁷⁾ Pirelli Labs SpA, Viale Sarca 222, 20126 Milan, Italy

Abstract

On the basis of the Yoshiaki Arata's "sauna bath reactor", a simplified reactor (one chamber, without the second internal hollow Pd chamber where the material to be studied is filled) has been built, capable of operating at high pressures (100 bar) and at temperatures from -196 up to 350°C. With this instrument various Pd containing materials were tested: Pd black, HSA Pd black, Pd on activated carbon, Pd (from nitrate) on colloidal silica, Pd in porous $\gamma\text{Al}_2\text{O}_3$, Pd-Sr nitrate in porous $\gamma\text{Al}_2\text{O}_3$. The D/Pd ratios have been measured in all the materials. Evidence of excess heat was found with some of the tested materials. The one chamber reactor was improved later by adding a second, reference chamber, which is similar to the working chamber, as a sort of *differential calorimeter*. Such a device is capable to highlight (and measure), in real time, the occurrence of excess heat in Pd powders or Pd containing materials put in the crucible of the measurement chamber of the instrument. With respect to the reference chamber, whose crucible is filled with inert material, the excess heat, due to the Deuterium absorption, makes the temperature of the working chamber to rise. Both the chambers are supplied with the same power input. A sample of Pd black_HSA (4.8 g) showed (at 290°C) a clear excess temperature of 13.5°C equivalent to an excess heat of up to 520 milliwatts. *The direct relationship between the excess heat and the D₂ content in the Pd powder has been demonstrated*: in fact, when a partial degassing of the Pd powder occurred, a subsequent decrease of the excess heat also occurred. The anomalous excess heat, due to the close interaction, at nanometric scale, of Deuterium with Pd, seems to be clearly detected by proper experimental set-up and operating conditions. The amount of energy detected is larger of any chemical reaction known.

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* E-mail: francesco.celani@lnf.infn.it

1) Introduction

In Condensed Matter Nuclear Science experiments it has been recently shown that *nano-structures* of specific elements (in particular Palladium) are the key materials for the generation of anomalous effects (both of chemical and/or nuclear origin).

In an experimental, and theoretical too, paper (Ref.1), Professor and Academician Yoshiaki Arata, one of the main experimentalists active in such a specific field, showed (and explained) that extremely large quantities of Hydrogen (H) or Deuterium (D) can be absorbed into nano-sized materials, even at mild H₂ - D₂ pressures (e.g. 10bar).

The main authors and the distinctive features of their experimental approaches, using nanostructures, are listed below:

1.1) Prof. Yoshiaki Arata; Osaka University-Japan; (Ref. 2);

Technology: metallurgical production of nano-particles;

since 1992; Pd_black: (mainly of commercial origin) particle size: 50-1000nm;

since 2002; [ZrO₂]₆₅-Pd₃₅: home made, intimate mixture (Pd size:10-15nm.);

1.2) Dr. Yasuhiro Iwamura; Mitsubishi Heavy Industries, Yokohama-Japan; (Ref. 3,)

Technology: thin layers (10-100nm) of Pd, CaO, Sr, Cs;

since 2000; mainly micro and sub-micro electronics methods (sputtering, ion beam deposition);

The nano-sized materials (layer by layer) are deposited on a thick layer of Pd (100μm), capable to stand heavy mechanical stress (temperature up to 80°C, pressure drop up to 3bar).

1.3) Dr. Francesco Celani and co-workers (National Institute of Nuclear Physics, Frascati-Italy); (Ref. 4).

Technology: electrolytic methods;

Fractal like surfaces ("roughness" 20-2000nm) were produced on thin (Φ=50μm) and long (100cm) Pd wires.

Behaviour and properties of the fractal like surfaces were explained since 2005 (Ref. 5).

2) Sauna bath reactor, energy source, ashes

On July 2005 Prof. Yoshiaki Arata introduced the "*Sauna-bath reactor*" (Ref. 2).

The experimental set-up and the obtained results were disclosed, for the first time, during the ICCF12 Conference, held at Yokohama (Japan) on November 24-December 2, 2005.

Since 1992, (Ref. 6, and reference therein), he was able to obtain, by electrochemical loading, extremely high D₂ – H₂ pressures in the hollow cavity (eventually filled with some materials) of a special thick Pd cathode (the so-called Double Structure Cathode). He noted that, when Pd micro or (better) nano particles were put inside the cavity, a surprisingly high loading ratios (D/Pd –H/Pd >1) could be obtained, even at an internal D₂ –H₂ pressures of few bars. In case of Deuterium loading, an anomalous heat generation was also observed.

In order to reduce the strong input power required for the electrolytic current (which could hinder the excess heat), he developed the "*sauna bath reactor*".

In the sauna bath reactor D₂, flowing through the walls of a Pd tube, enters the internal part of the tube (the "cavity"), maintained at few hundred degrees °C, without applying external

energy (like electrolysis): even few bars of D₂ external pressure (the tube is completely surrounded by a sealed SS vessel) are enough to ensure a fast diffusion into the cavity. Moreover, the D₂ gas passed through the Pd tube is extremely pure and at the inner surface of tube is in the atomic form (D₀), easy to be absorbed by any kind of Pd (or Pd alloys) micro or nano particles located in the cavity.

The input power necessary to ensure the required temperature (100-200°C) of the system, according to our experience with a similar apparatus (total volume: 30-50 cc), is of the order of 2-6W and depends on such main experimental factors, as following:

- a) intrinsic geometrical aspects of reactor;
- b) thermal conduction losses due to connection tubes;
- c) thermal conduction losses due the thermometer put inside the powders;
- d) heat losses due to both convective motions (mass transport) and high thermal conductivity (about 0.15 W/K*m at NTP) of pressurised D₂,
- e) *performances of the thermal insulation (W/K*m) material adopted.*

Further advantages of the sauna bath approach are:

- a) no consumption of expensive electrolytes (like D₂O). In principle, only D₂ gas has to be filled at the beginning of the experiment and small amounts of D₂, proportional to the excess energy produced, are required for refilling.

* It is note worthy that Arata, in dedicated experiments with Pd_black at High Surface Area (HSA) or Pd-ZrO₂ nano-particles, both loaded under pressurised D₂, was able to detect quite large amounts of ⁴He and even, well measurable, amounts of the extremely rare ³He. In fact, at the end of the experiment, it was possible to extract, by under vacuum diffusion, all the Hydrogen isotopes (H₂, D₂, T₂) present in the cavity: ³He and ⁴He, which cannot diffuse through the Pd walls, remained in the cavity. By connecting the cavity with a high resolution Quadrupole Mass Spectrometer, Helium isotopes can be analysed without the heavy interference of large amounts of D₂.

- b) Explosive recombination of D₂ with O₂ is avoided (e. g. reaction $2D_2+O_2\rightarrow 2D_2O$, specially when sheets of Pt_black catalyser are used at the top of, tightly closed, electrolytic cells);

- c) It is possible to detect even modest excess heat: the input power necessary for the warm-up of the studied material up to the “trigger temperature”, can be kept fairly low by using high quality materials for the thermal insulation.

2.1) The problem of reactions for excess energy.

We recall that exist several theoretical models that try to explain the observed production of excess heat, and related ashes, by Deuterium-Pd systems.

To enter further in this argument, still now open, we recommend reading the comprehensive paper of Prof. Akito Takashi (Osaka University) presented at this Conference (Ref. 7).

3) Frascati-INFN activity in the powder nano-particles technology.

The experimental activity started on July 2006.

3a) Taking into consideration the advantages of the Arata's reactor, we decided to build up a simplified version (i.e. without the inner Pd tube) of the sauna bath reactor (all parts in AISI 304 and 316 SS), capable to operate at high pressures (100bar) and at high temperature (320°C).

The apparatus consists of two extruded SS tubes (V_1 and V_2 chambers) with external-internal diameters of 12-10mm. Only one chamber, the V_2 , is filled with material to be studied and can undergo thermal cycles. It was called the One Chamber Reactor (OCR).

The Pd micro or nano particles were put inside a small (SS) crucible, located in the reaction chamber V_2 . Starting from the external surface of the SS tube in V_2 , a cascade of fibre-glass insulation wool sheets provides for thermal insulation. The bottom of reaction chamber V_2 (where the SS crucible is located) was further screened by means of several layers of thin Al foils (thickness 15 μ m), as thermal radiation reflectors, and kapton.

The whole set up was put inside a glass Dewar, surrounded by a plastic insulating foam.

The V_1 chamber, maintained at room temperature, serves as D_2 storage; proper valves can interconnect the two chambers. The V_2 chamber, containing the crucible filled with the powders to be studied, can be heated by a DC power supply. The volume of each chamber is 35cc. Further details of experimental set-up are the following:

- d) The joule heater used in the reactor chamber V_2 is made of a Constantan wire, a Cu-Ni alloy whose electrical resistance remains almost constant in the temperature range of 20-400°C, coiled around the SS tube;
- e) The heater is fed by a constant voltage stabilised power supply. The value of voltages (four contacts measurement method) and the currents flowing in the Cu-Ni resistor are digitalised (by a high resolution, 6.5 digits, ADC) and acquired/stored by the on-line computer (acquisition system Lab-View type): calculation of input power.
- f) The usual acquisition time of all the parameters of the experiment (5 temperatures, 2 pressures, 2 or 4 voltages, 1 current) is 10 seconds.
- g) Pipes connectors, valves, etc. are of Swagelock standard.

* For simplicity, the anomalous thermal effects, at this stage of experimentation, have been detected by the *isoperibolic methods*.

* The anomalous thermal effects could be evaluated by comparing the equilibrium temperatures (at a given and constant power input) of the reaction chamber (V_2) when filled either with D_2 or with an inert gas, at the same pressure. ^4He was used as inert gas: its thermal conductivity (0.142W/K*m at NTP) is quite similar to that of D_2 .

Both the chambers (volume 35cc) were equipped with very sensitive and accurate electronic pressure gauges, in order to evaluate the D/Pd ratio from the corresponding pressure drop.

3b) Tested materials; D/Pd ratio; evidences of thermal anomalous effects.

3b.1a) "Standard" Pd black (Aldrich); 2g; measured (by SEM) few particles with $\Phi=300-1000\text{nm}$, most larger (several micron); the powder, at the beginning of the experiments, was previously baked at: 140°C, 12h, under vacuum (rotative pump equipped with a liquid nitrogen trap; pressure 10^{-3}mbar).

All the tested materials have been treated at T_{\max} : 220°C; P_{\max} : 25 bar.

Results:

- * $D/Pd=0.85$ at 8 bar was achieved;
- * Very weak thermal effects were detected.

3b.1b) Pd black “High Surface Area” (Engelhard→Aldrich); 2g; measured (by SEM) several particles with $\Phi=50-300\text{nm}$; baked at 140°C, 12h, 10^{-3}mbar ; T_{\max} : 220°C; P_{\max} : 25 bar.

Results:

- * $D/Pd=0.90-0.95$ (at 8bar);
- * Weak thermal effects, little better in respect to the “standard” Pd black were detected; heavy sintering problems appeared after D_2 absorption and repeated cycles from high to room temperatures.

3b.2) Pd on activated Carbon; Pd=5% weight; 5g; $\Phi=50-100\text{nm}$; baking up to 190°C, 12h, 10^{-3}mbar ; T_{\max} : 220°C; P_{\max} : 25bar. Very old material (prepared over 20 years ago).

Results:

- * $D/Pd=0.9-1$;
- * Weak thermal effects and difficulties to eliminate water and/or other gas previously absorbed by carbon.
- * The D/Pd ratio close to 1 can be due to some D_2 physioabsorption in the activated carbon.

3b.3) $Pd(NO_3)_2$ in HNO_3 (10% weight) mixed with porous (nanometric size 4-5nm) colloidal silica (Pd=20% weight; SiO_2 80%); 5g; T_{\max} 300°C; P_{\max} : 25bar.

Results:

- * $D/Pd=1-1.2$ at 10 bar;
- * Not stable anomalous thermal effects have been detected; excess heat seems to depend, very strongly, on the Pd-silica preparation procedures. The material is promising but very large systematic work is needed.
- * The D/Pd ratio larger than 1 can be explained as due to the *spillover effect*

3b.4a) γAl_2O_3 (Φ of holes=5.8nm, Aldrich) mixed with $Pd(NO_3)_2$ in HNO_3 (10% weight). γAl_2O_3 80% Pd 20%; total weight 5g; T_{\max} 300°C; P_{\max} : 75bar;

Results:

- * $D/Pd=1.4-2.0$ at 10bar;
- * Non-stable, anomalous thermal effects were detected; sintering problems appeared after high-low-high cycling temperatures.

3b.4b) γAl_2O_3 83.3% (Φ of holes=5.8nm, Aldrich) mixed with $Pd(NO_3)_2$ 13.3% + $Sr(NO_3)_2$ 3.3%

total weight 5g; T_{\max} 320°C; P_{\max} : 75bar;

Results:

- * $D/Pd=2-5$.
 - * The very large D/Pd ratio can be explained only by the *spillover effect*.
 - * *Strong indications of excess heat, but not enough stable for long time.*
- Reduced sintering problem with respect to 3b.4a), but still present.

4) Operative procedure (as at April 2007) for the preparation of the $\gamma\text{Al}_2\text{O}_3$ -Pd-Sr mixtures

4.1) Total weight of, as received, $\gamma\text{Al}_2\text{O}_3=20\text{g}$

4.2) Drying.

The $\gamma\text{Al}_2\text{O}_3$ (Aldrich, Φ of holes=5.8nm) was put in a quartz crucible inside a quartz tube of a programmable oven (e.g. Barnstead Thermolyne, mod. 21100). The features were:

- * Temperature ramp-up ($T_r = 0.3^\circ\text{C}/\text{min}$);
- * Dwell time (T_{dw} , at maximum temperature, 600m);
- * Temperature maximum, T_{max} ($T=25 \rightarrow 130^\circ\text{C}$);
- * Atmosphere: vacuum ($5 \cdot 10^{-3} - 1 \cdot 10^{-2} \text{mbar}$) by rotary pump with LN_2 trap
- * Cooling spontaneous.

4.3) Wetting and Mixing:

- * 10.000g (from the original 20g) of dried $\gamma\text{Al}_2\text{O}_3$.
- * Home made solutions of $\text{Pd}(\text{NO}_3)_2$ in 10% weight HNO_3 (Pd content = 0.2g/cc) and a $\text{Sr}(\text{NO}_3)_2$ solution (in H_2O) with Sr content 0.2 g/cc were prepared.
- * 8cc of the Pd solution were mixed with 2cc of $\text{Sr}(\text{NO}_3)_2$ solution: *mother solution*.
- * 3cc (over 10 total) of Pd-Sr *mother solution* were drop-by-drop poured on 10g of the $\gamma\text{Al}_2\text{O}_3$ powder, in a glass beaker, under a continuous mixing by a glass stick. Such a procedure is usually known as *incipient wetting impregnation*. With respect to the “standard” incipient wetting procedure, we reduced the amount of liquids from about 5 to 3 cc.

4.4) Drying (*water and HNO_3 elimination*).

The wet material (HNO_3 , H_2O) was heated in the quartz tube furnace. Vacuum is made by a high quality water pump ($P_{limit}=32\text{mbar}$; usually operated at 100mbar) because of corrosion problems due to the presence of HNO_3 vapours. Connection tubes in PTFE.

Furnace operating conditions: $T_r=0.3^\circ\text{C}/\text{m}$; $T_{dw}=600\text{m}$; $T=25 \rightarrow 130^\circ\text{C}$; spontaneous cooling under vacuum.

4.5) 3cc of the mother solution were, drop by drop, poured again on the mixture, according to the previously described incipient wetting impregnation. Drying operations as mentioned above.

4.6) All the described operations were repeated, by dropping each time 2cc of mother solution, until the 10cc are finished.

4.7) Calcination

The powder, in the quartz crucible, was heated in the quartz tube furnace.

Operating conditions: $T_r=1^\circ\text{C}/\text{m}$, $T_{dw}=1050\text{m}$; $T_{max}=450^\circ\text{C}$ (for short time up to 500°C).

Atmosphere (vacuum):

- * $T_{dw}=0-250\text{m}$; water pump (i.e. total time of water pumping, from the beginning of calcination step), is about 680m.

After 200m of Tdw, fresh air, for about 10m, was allowed to enter the quartz tube, by continuously pumping out at about 800mbar. Then, the pressure was reduced to 100mbar in static conditions: when the temperature is increased from 450°C ($T_r=5^\circ\text{C}/\text{m}$) up to 500°C for short time, observe if some red colour gases (due to decomposition of Pd nitrate) are still visible. If not, reduce again the temperature to 450°C; otherwise, remain at 500°C until, after repeated “washing” operations, all the red gasses disappeared.

* Tdw=250-550m → 2 stages membrane pump (PTFE type, 20mbar);

* Tdw=550-1050m → rotary pump with LN2 trap ($5 \cdot 10^{-3}$ - 10^{-2} mbar).

4.8) Check the weight.

The weight should be about 12.8g; in fact:

Al_2O_3 : 10.00g;

PdO: (Pd=1.6g+ O=0.24g) = 1.84g;

$\text{Sr}(\text{NO}_3)_2$: (Sr=0.4g+(NO_3)₂=0.56g)= 0.96g.

5) Deuterium loading in V₂.

5.1) PdO reduction.

D₂ gas was allowed to enter the reactor (maintained at 140°C), at low pressure (1bar) and at a very slow flux in order to avoid excessive self-heating (and, as consequence, sintering of Pd nano-particles).

PdO is reduced to metallic Pd according to the reaction: $\text{PdO} + \text{D}_2 = \text{Pd} + \text{D}_2\text{O}$

In order to eliminate the D₂O formed in the reaction chamber, several cycles are performed of D₂ intake and subsequent vacuum purging by rotary pump.

Final drying, of possible residual water, by vacuum pumping (12h) at 250°C (rotary pump and LN2 trap, at about $5 \cdot 10^{-3}$ mbar).

5.2) Pd loading by Deuterium.

Pd loading is performed at room temperature. The D₂ absorption (D/Pd ratio) can be evaluated by the pressure variation in the D₂ storage chamber (V1); an accuracy within 2-5% can be achieved, with electronic Gauge pressure sensors (from GEMS Company) having a sensitivity of 0.25% of Full Scale.

In order to maximize the accuracy of D/Pd ratio, 2 sensors, the first one with FS=100bar and the second one with FS 25bar (with proper valve) were used.

The Pd loading procedure is explained step by step hereinafter:

- Make vacuum on chambers V1 and V2.
- Close the connection between V1 and V2 and fill with D₂ gas the chamber V1 (usually 25bar);
- A 0.5 cc volume chamber, located in between V1 and V2 chambers, (see Fig. 1) allows for a very slow passage of D₂ into the reaction chamber.
- Wait for thermal equilibrium in V2 (the temperature should increase because of the D₂ absorption by the Pd powder (exothermic). Measure the equilibrium temperature of V2.

- If necessary, refill (as many times as necessary) the V1 chamber with D2 gas at high pressure (usually 100bar) and load again V2 up to the pressure stated (recently up to 60-70 bar).

5.3) D/Pd measurement.

The abbreviation used are as following:

P_1 = Absolute Pressure of chamber V1 (before connection with V2);

V_1 = Volume of Chamber V1;

T_1 = Temperature of Chamber V1 (before connection with V2);

P_{1F} = Absolute Pressure of Chamber V1 (after connection with V1);

V_2 = Volume of Chamber V1;

T_2 = Temperature of Chamber V2 (after connection with V1);

R= molar constant of gas

* The initial moles n_1 of D₂ gas, in V₁, are:

$$n_1 = (P_1 * V_1) / (R * T_1) \quad (1)$$

* The final moles N_{2F} of D₂ gas, after absorption by Pd powders, are:

$$n_2 = [P_{1F} * (V_1 + V_2)] / [R * (T_1 + T_2) / 2] \quad (2)$$

* The moles (ΔM) of D₂ gas absorbed are:

$$\Delta M = n_2 - n_1 \quad (3)$$

* If M_{Pd} are the moles of Pd used, the D/Pd ratio is:

$$D/Pd = 2\Delta M / M_{Pd} \quad (4)$$

REMARK

The amount of Deuterium is evaluated as “ideal” according to gas law (correction only by temperature) up to pressures of 10bar (undervaluation of about 1%). For larger pressures, were applied the proper Van der Walls corrections. In a future paper we will give more details about such important aspect and proper analytic fitting equations that we developed recently for such purpose.

6) Evaluation of the thermal anomalies.

When the Pd loading process is completed, the temperature of the V₂ chambers is made to increase.

The heater power (watt) is step like controlled:

$$0 \rightarrow 3w \rightarrow 0 \rightarrow 4w \rightarrow 0 \rightarrow 6w \rightarrow 0 \rightarrow 8w \rightarrow 0 \rightarrow 12w \rightarrow 0.$$

Anomalous heat generation is evaluated by measuring the equilibrium temperature of the V₂ chamber against the equilibrium temperature measured in previous calibration runs, when the Pd powder was kept under inert gas atmosphere (usually ⁴He).

The dissipated power in the V_2 chamber normally increases by increasing the gas pressure in the chambers. That is because D_2 (or 4He) works as an exchange gas from the hot area (close to the heater), to the coldest one (at room temperature). This effect is presented in Tab. 1.

Table 1. File 11apr07. One Chamber Reactor (OCR). Relationship between the temperature inside the crucible (TV2) and pressure applied. For completeness are reported also the temperatures of Joule heater and room.

Timer s	TV ₂ °C	TH ₂ °C	Troom °C	Pressure bar	TV2 - Troom °C	TH ₂ - T _{room} °C	TV ₂ – TH ₂ °C	Note
166000	234	257.8	21.9	62.6	212.1	235.9	-23.8	D ₂ , material partially active
241700	254.6	274.8	20.6	18.7	234	254.2	-20.2	“
331500	253.4	273.8	21.6	5.8	231.8	252.2	-20.4	“
332300	253.4	274.1	21.9	1.16	231.5	252.2	-20.7	“
414300	235.8	275.4	21.8	0	214	253.6	-39.6	Vacuum
420900	251.3	274.4	22.3	1	229.0	252.1	-23.1	Air

In Tab. 1 (experiment started on 11Apr07) the temperature dependence (versus pressure) of the reactor chamber is shown (input power 6.04W), when the γAl_2O_3 -Pd-Sr(NO₃)₂ powder was only “partially active”. It was used a high quality Dewar (WKG, Germany) that, unlikely, can’t be used at effective Dewar wall temperature larger than 200°C.

The pressure effect is significant and can’t be neglected, in particular if small amounts of excess heat are to be detected. It is therefore necessary to perform calibration runs not only at different input powers but also at different pressures both with D_2 and 4He .

By considering the fact that the thermal conductivity of H_2 (similar to D_2) varies, at 500K, of only +1.8% starting from 1bar up to 100bar (i.e. from 0.2661 to 0.2711 W/m*K), we have to argue that the large value (+6.4%) of thermal leaks due to pressure variation (up to 64bar) is due, mainly, to convective motion of gas. As a consequence, some work has to be done, in the near future, to our experimental set-up in order to reduce such large detrimental effect.

Regarding the data shown in Tab. 1, it should be noted that (timer 323300) the TV₂ – Troom is 231.5°C; by replacing the D_2 atmosphere with air, at the same pressure (1 bar), the TV₂ – Troom dropped to 229.0°C. According to our previous experience, the variation of temperature when D_2 (1 bar) or 4He is replaced by air (1 bar) should be practically negligible. The registered difference of 2.5°C is supposed to be due to some residual activity of the Pd powder even at very low pressure of D_2 .

6.1. Differential calorimeter.

It is well known that, in CMNS experiments, the eventual generation of excess heat is seen with scepticism and the experimental data are often strongly questioned. We realised that because of the troublesome and delicate operations necessary for the calibration of our reactor and because of the pressure effect, our experimental results could be often criticised and sometime even refused. Accordingly, in order to prevent as much as possible any criticisms and objections, we decided to modify our reactor in such a way as to eliminate both the need of the calibration runs and the hardly controlled pressure effect.

At the end of May 2007, the chamber V_1 was equipped with the Constantan Joule heater, the insulation layers and the glass Dewar, so to match as much as possible to the reaction chamber V_2 .

The resistance value of the Constantan wire in the chamber V_1 (previously used in the OCR configuration as “storage chamber”) was made the same that in V_2 ; the two resistances are connected *in series* so as to be crossed by the same current (i.e. both the chambers were supplied with the same input power).

In this way a sort of *differential calorimeter* was assembled (Fig. 1), capable to detect, in real time, any anomalous heat generation between the active material (in V_2) and the inert one (in V_1) under the same conditions of temperature and D_2 pressure.

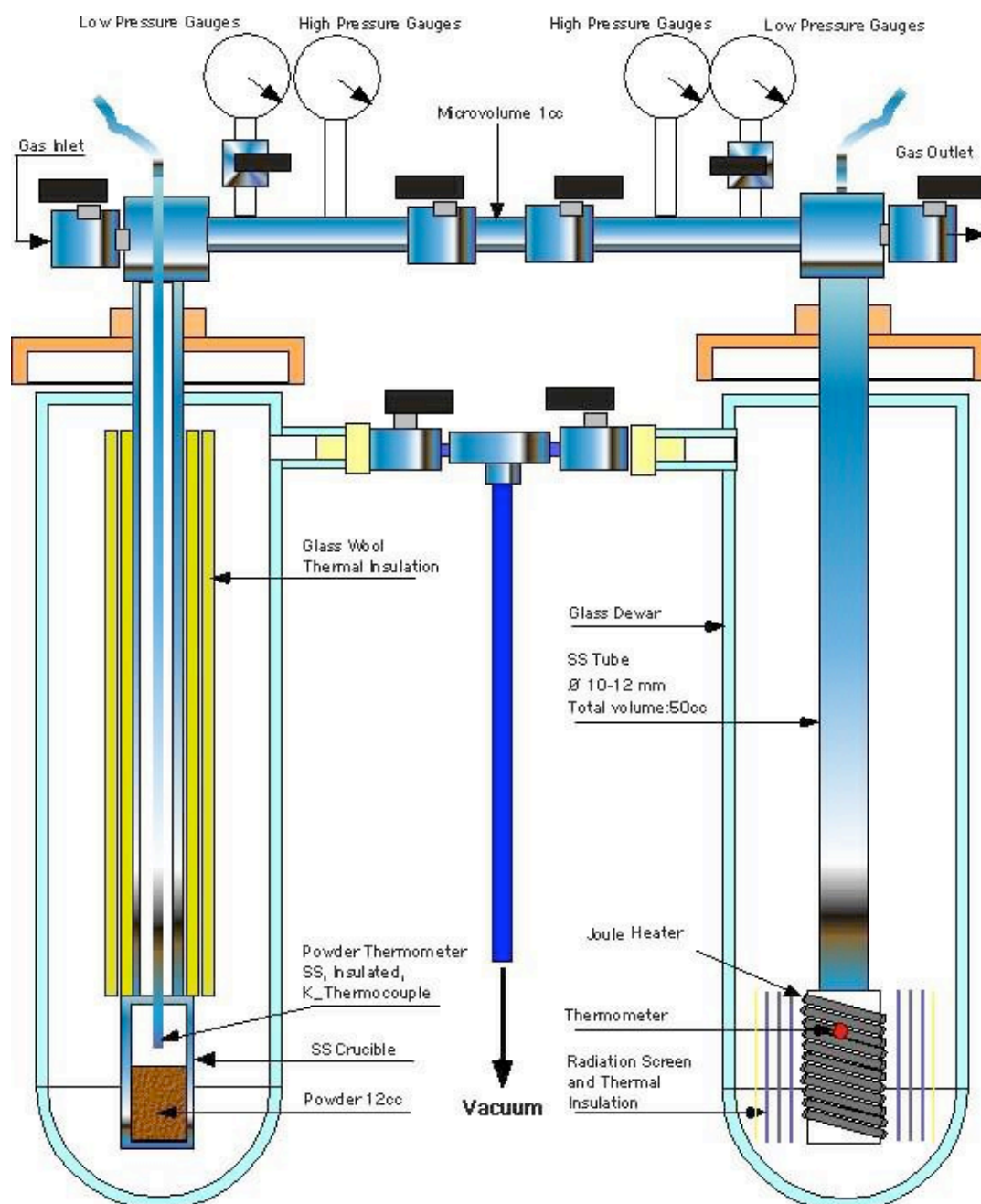


Fig.1. Schematic of differential calorimeter.

In preliminary runs with inert material we observed that, at constant input power, when the equilibrium temperature has been reached, the difference of temperature between the two chambers was very small ($< 1^{\circ}\text{C}$). In these conditions the amount of the excess heat, eventually generated in V_2 , could be easily estimated conservatively (i.e. supposing that the dissipations do not increase at the increasing of the temperature), through a simple proportion, as following:

- * W_H = constant input power at the heaters (watt)
- * T_1 = equilibrium temperature in V_1 ($^{\circ}\text{C}$)
- * T_2 = equilibrium temperature in V_2 ($^{\circ}\text{C}$)
- * δw =excess heat (watt)

As a consequence:

$$W_H/T_1 = (W_H + \delta w)/T_2 \quad (5)$$

$$\delta w = W_H \cdot (T_2 - T_1) / T_1 \quad (6)$$

Moreover, if the electric input power (by the Joule heater) to the two chambers isn't exactly the same, the equivalent temperatures differences can be corrected using chamber V1 as reference for calculations.

6.1) Pressure effects.

In the differential calorimeter the pressure effect is negligible only when the two chambers are at the same pressure (i.e. the connection valve is on). In some cases (connection valve off) it could be very interesting to examine what is happening in the V₂ chamber (i.e. a possible degassing of the Pd powder and, consequently, a sudden increase of pressure in V₂).

In order to achieve a complete knowledge of the pressure effect an experimental campaign was performed with the new differential calorimeter.

The crucible in V₁ was filled with (previously vacuum dried) pure $\gamma\text{Al}_2\text{O}_3$ (5.5g); the atmosphere was always D₂ gas. In all the experiments the input power was maintained constant (12 watt).

The results are summarised in Tab. 2.

Table 2. File14giu07. Differential calorimeter. Temperature-pressure dependence.

TV ₁ (°C)	TH ₁ (°C)	Troom (°C)	Pressure (bar)	TV ₁ -Troom (°C)	TH ₁ -Troom (°C)	TV ₁ -TH ₁ (°C)
281.3	276.8	25.0	74.4	256.3	251.8	+4.5
287.7	282.0	26.2	63.3	261.5	255.8	+5.7
295.9	288.3	25.6	46.88	270.3	262.7	+7.6
300.5	291.6	23.1	30.85	277.4	268.5	+8.9
305.6	295.9	24	20.43	281.6	271.9	+9.7
305.1	295.1	24.6	11.71	280.5	270.8	+10.0
305.8	296	25.9	6.8	279.9	270.1	+9.8
279.6	295.6	24.2	0	255.4	271.4	-16.0

New tick-wall Dewar (2.2mm), not silvered: it can withstand temperatures up to 350°C.

New SS crucible (volume 12cc) with thick wall (2mm). Chamber V1 volume=50cc.

Material: dried γ Alumina. Gas: Deuterium. Power: 12W.

TV₁ is the temperature measured inside the crucible filled with the γ Alumina powder.

TH₁ is the temperature of the Joule heater, measured outside the SS chamber, and inside the Dewar.

The best heat transfer efficiency is at about 20bar (TV₂ - Troom=281.6°C). By reducing the pressure (from 20.43 to 6.8bar) small variation of temperature is observed ($\Delta T/\Delta P = +0.12^\circ\text{C}/\text{bar}$); the decrease of temperature tends to be more and more important as far as the pressure exceeds 20bar (20.4 → 74.4bar; $\Delta T/\Delta P = -0.47^\circ\text{C}/\text{bar}$).

As expected, the worst condition of the heath transfer efficiency is in the vacuum condition (255.4°C).

The results are qualitatively similar to the previous OCR.

7) Results

In this paper are shown the results obtained with the differential calorimeter in a complex and long (over one month) experiment.

According to our previous results with the OCR, we tested, at first, a sample of HSA (High Surface Area) Pd_black powder, by Engelhard → Aldrich (cod. 520810-5g): it gave indications of some excess temperatures even at low D₂ pressures (<25bar). Same batch of production.

Apparent density: 4.8g/9cc=0.53g/cc

The amount of material was 4.8g (0.2g was kept as a reference).

The powder (put into the V₂ crucible) was previously degassed-baked (15h in vacuum by a rotative pump equipped with LN₂ trap at 110°C; in the previous experiments with OCR the temperature was 140°C and time 12h).

After cooling to room temperature, D₂ gas was fed in micro-steps so as to avoid that the powder temperature should exceed 55°C. The temperature measurement was made using a K type thermocouple, SS covered, with a diameter of 3mm and put inside the powders. The tip of the thermometer is at a distance of 2cm from the bottom of the crucible.

The measured D/Pd ratio, at 8.7bar and 35.5°C, was >0.92. Such value increases to >0.96 when the effects of water content and of other impurities in the Pd are taken into account.

The D₂ pressure was increased up to 64bar at 30°C.

In order to detect any eventual degassing of the Pd powder the connecting valve between the two chambers was off.

The variation of pressure (P₂–P₁) is shown (in Fig. 2, 3, 4, 5) by the *bright-blue* line.

The temperature gain (ΔT₂₋₁ in the following) between the working and the reference chambers is in *orange*.

The *green* line shows the temperature gain ΔT_{2-1p} corrected for the variation of pressure (P₂–P₁), according to the data presented in Tab. 2 (effect of pressure). Such effect is macroscopic only for pressure larger than 20bar and has a negative slope (about -0.47°C/bar).

The absolute pressure (in V₂) is in *dark-blue*.

The temperature of the V₂ chamber is in *red*.

In order to see the results of the long time lasting experiment with enough resolution, it was divided in 4 Figures (2, 3, 4, 5), and each Fig. has some peculiarities, as shortly resumed:

- Fig. 2. File 19giu07. D₂. Starting of the experiment and several cycles 0→12→0W.
- Fig. 3. File 07lug07. D₂ → Vacuum → ⁴He. Under D₂, increased the power 12→14→16W: detected D₂ degassing and reduction of excess temperature. With ⁴He the excess temperature went to 0°C.
- Fig. 4. File 13lug07. Several tests, at variable power, with ⁴He (p=5.8bar@RT).
- Fig. 5. File 19lug07. Loading D₂ from LN₂: no improvements of results. Larger degassing and related reduction of excess temperatures in respect to Fig. 2 and 3. Pressure reduced 80→30→18bar: the degassing increases and excess temperature vanish.

End of the experiment.

7.1) Fig. 2.

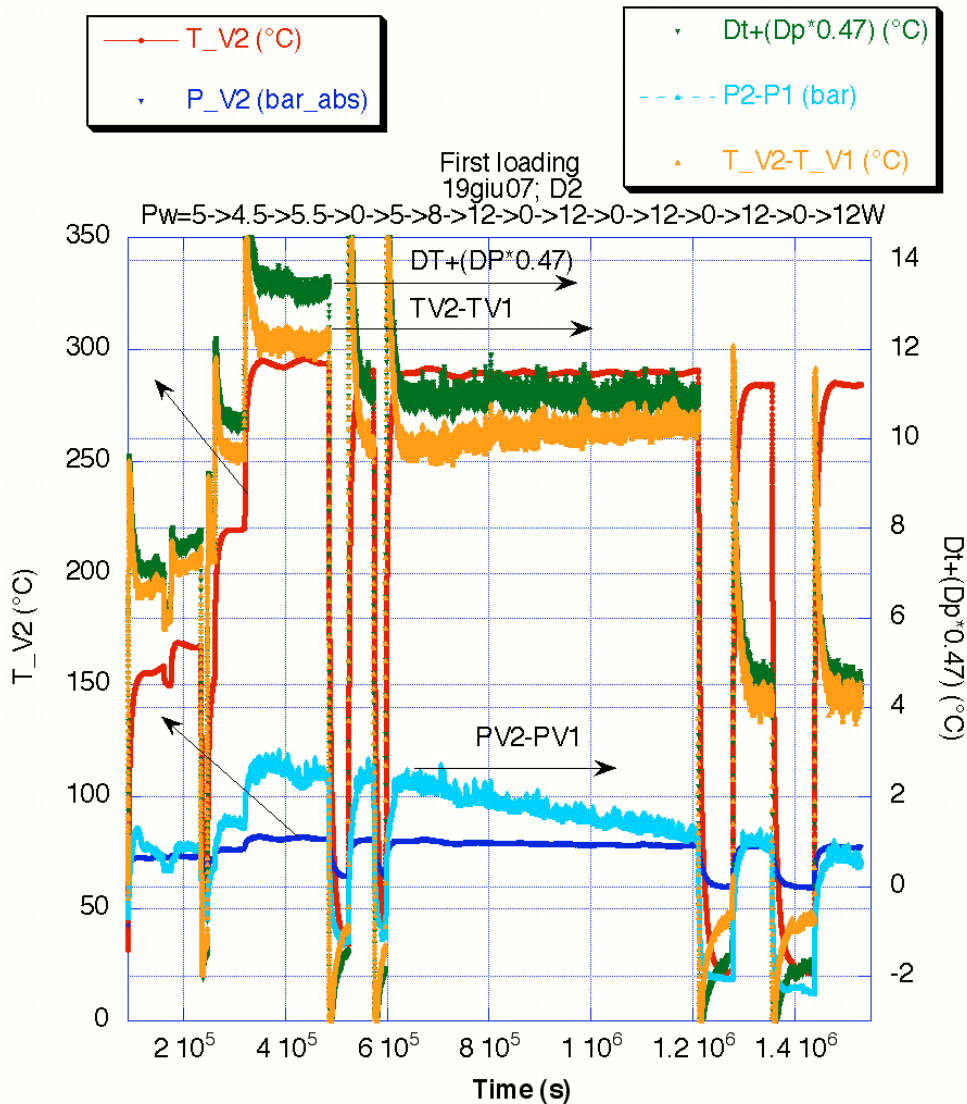


Fig. 2. File 19giu07. Results with differential calorimeter. First loading and warming up. At the beginning of the experiment the heaters were supplied with 5 → 8 → 12 watts of input power. The temperature gain $\Delta T_{p_{1-2}}$ in V_2 increased (7 → 10.5 → 13.5°C). The excess heat, accordingly, was 220 → 380 → 520mW.

At $5 \cdot 10^5$ seconds the input power was switched off and then applied again. The temperature gain $\Delta T_{p_{1-2}}$ in V_2 dropped from 13.5°C to 11°C (green lines).

At about $1.2 \cdot 10^6$ seconds the input power was again switched off for a longer time: the temperature gain $\Delta T_{p_{1-2}}$ in V_2 (4.5°C) dropped down dramatically.

Switching off the power, and subsequent cooling, seems absolutely to be avoided.

It can be seen that the D_2 pressure in V_2 (blue line) slowly decreases, because of a small leak. The data shown were corrected for such (small) effect.

7.2) Correlation between excess power and operating temperature.

The almost direct correlation between the Pd powder temperature and the excess heat generation could be explained as follows.

Taking into consideration the well known Pd-D phase diagram, it appears that, by increasing the temperature, also increases, almost in a proportional way, the amount of β phase to the detriment of an equivalent amount of $\alpha + \beta$ phase. It seems therefore that a correlation would exist between the percentage of the β phase actually present in the Pd black and the amount of the generated excess heat.

7.3) Fig. 3

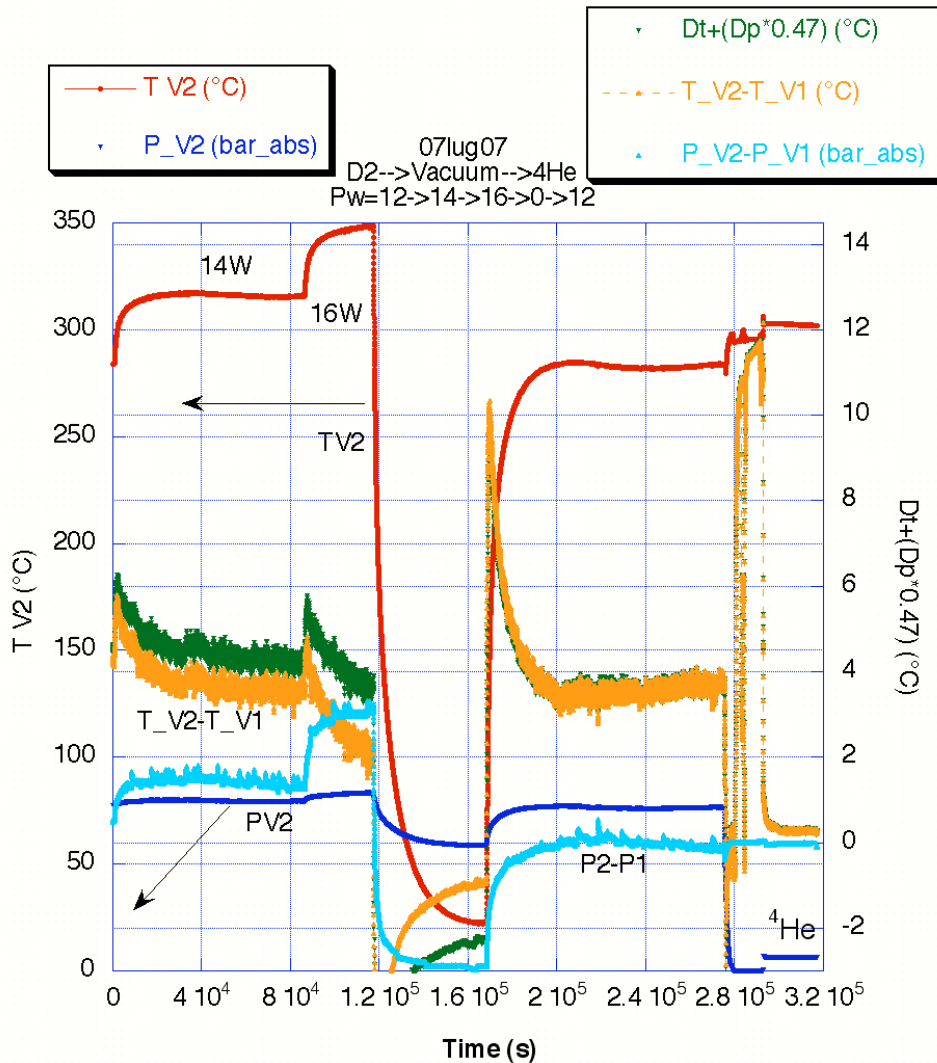


Fig. 3. File 07lug07. Results increasing the cell temperature up to 320 and 350°C. Later, time 275000s, made vacuum and added ^4He . The excess temperature vanished.

In Fig. 3 the input power was increased (12→14→16 watt). Descending slopes of excess temperatures. The $\Delta T_{p_{1-2}}$ tends to decrease; at 16 watt of input power, abruptly, the V_2 pressure raises up (large D_2 degassing) and the $\Delta T_{p_{1-2}}$ drops down.

This fact is of a paramount importance; in fact, (see the Fig.2) by increasing the powder temperature, the $\Delta T_{p_{1-2}}$ also increases. In correspondence of the powder degassing *vice versa*, the $\Delta T_{p_{1-2}}$ decreases. The relationship between $\Delta T_{p_{1-2}}$ and the D/Pd ratio appears to be very clear.

After a prolonged switching off, the input power was turned on (12W); the ΔT ($\cong 4^\circ\text{C}$) showed an ascending trend. At this point, in order to ascertain that the differential calorimeter was

working well (i.e. that the observed ΔT_{p1-2} was simply due to an accidental offset occurred along the time to the calorimeter), the “active” D_2 atmosphere was replaced, after vacuum degassing, by the inert 4He in both the chambers (connecting valve on).

Null gain of temperature was expected and null ($<1^\circ C$) was found:
the previous excess temperature results, shown in Fig. 2, have been validated.

7.4) Fig. 4

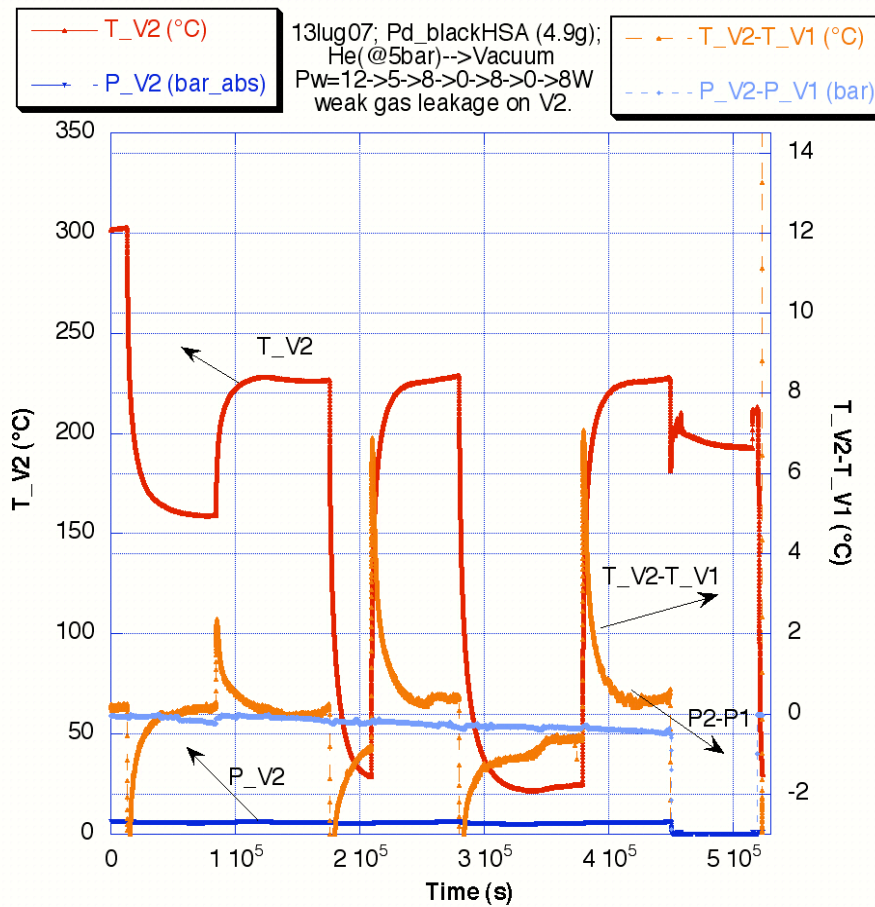


Fig.4. File 13lug07. Experiments with 4He at variable powers (12, 5, 8W).

Never excess temperature was found with 4He . The green line, that accounts of pressure effects, because very similar to orange one, was omitted for clarity.

7.5) Fig.5

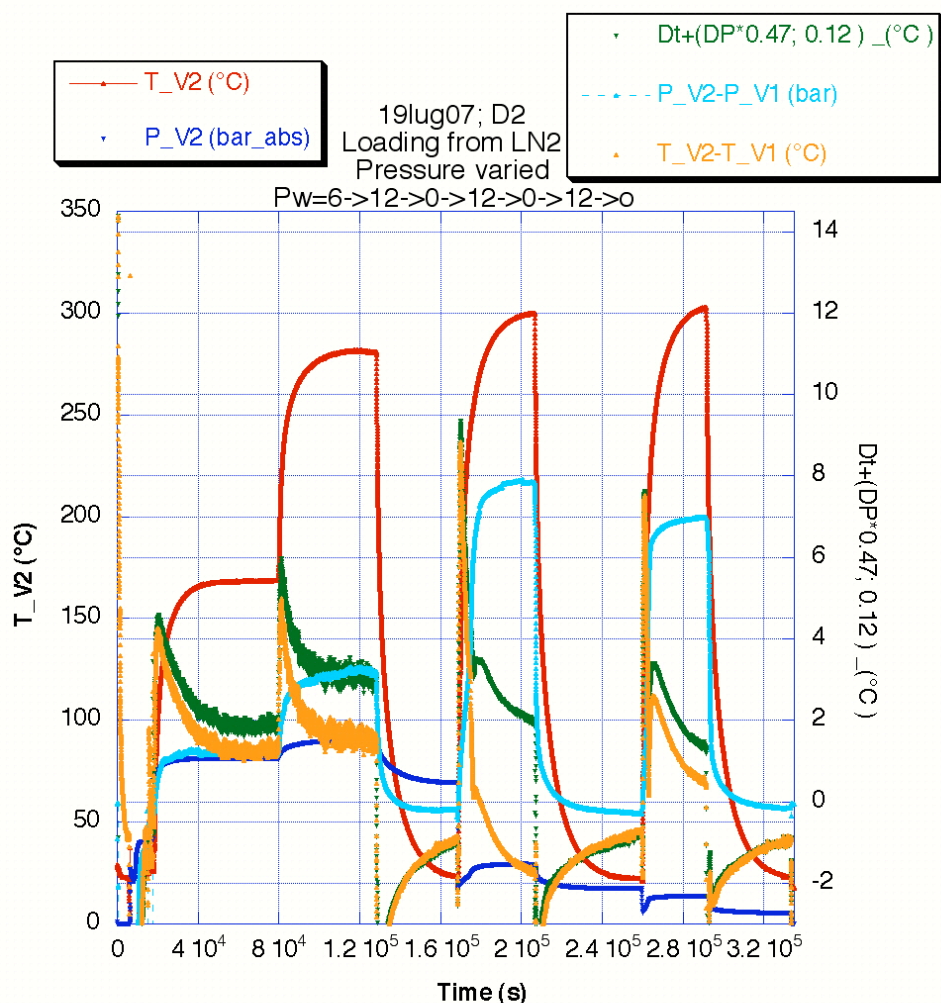


Fig. 5. File 19lug07. Experiment with loading D_2 from LN2. The pressure was decreased, at time 165000, from 70 to 18bar; at time 255000 the pressure was decreased from 18 to 6bar.

The loading from LN2 didn't have any practical effect. There is some excess temperature that decreases when the pressure was reduced and the deloading was large. Can be interesting to study the LN2 effect using virgin material, not damaged one as in this specific experiment.

It is important to remark that, at the end of the experiment, the visual aspect of the Pd black powder in the crucible was consistently modified, having passed from the original dark black colour to a silver like one.

In Fig. 6 is shown, by SEM micro-photography, the typical aspect of Pd_black after the experiment. We recall that the PD_black HSA we used, according to the specifications of the Company that sell it, has dimensions (for 10% of the volume of material) $< 5.8\mu\text{m}$. We measured particles even in the range of 100nm in the virgin material.

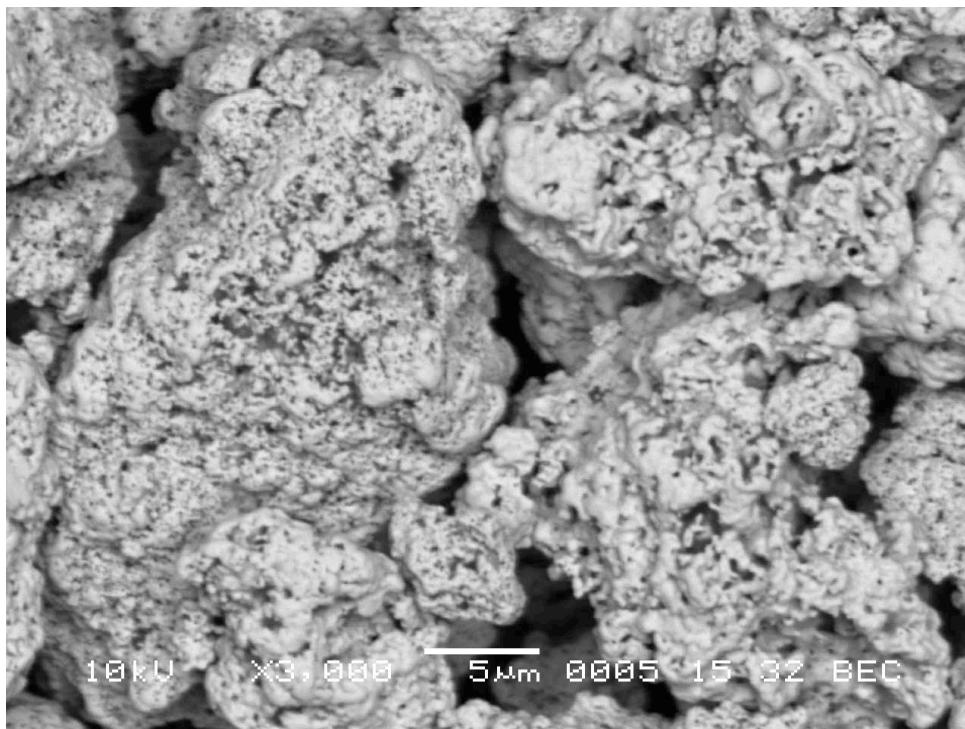


Fig. 6. SEM photograph of Pd_black_HSA at the end of the experiment.

It is evident that a sintering process of the Pd grains occurred along the time. The observed degassing of the Pd powder, and the consequent, sudden, drop down of the temperature gain, allows to suppose that the “activity” (i.e. the ability to produce excess heat) of the Pd nano-particles could be associated with their ability (with respect to the bulk) to prevent, up to a relatively high temperatures, the D₂ degassing.

8) Conclusions

It has been definitely demonstrated that micro and, in particular, nano particles of Pd can absorb Deuterium gas up to D/Pd ratios >1 at pressure of about 60bar.

The new developed differential calorimeter seems to be the ideal instrument for highlighting and evaluating the excess heat produced in the working chamber. It has been shown, by operating with a High Surface Area Pd black (D/Pd ratio>0.96 at 35°C and 8.7bar,) that the excess heat increases with the Pd temperature. This fact was interrelated with the increase of the percentage of the β phase occurring when the Pd temperature increases. The anomalous heat generation seems to be associated to the ability of the Pd nano-particles to prevent the D₂ degassing even at high temperatures. It has been demonstrated that, when a degassing occurs, a strictly correlated decreasing of the excess heat also occurs.

The amount of total energy produced was so large (about 500kJ) that the origin of excess energy can't be of chemical origin, taking into consideration the amount of Pd used (4.8g, i.e. 45mM). The amount of energy produced by use is about 10 times larger of most energetic chemical reaction known.

The results with Pd-black_HSA are in qualitative agreement with the results reported in Ref. 2. The temperature gain, larger in our experiments at the beginning, can be explained because one or more of the following reasons:

- a) Larger amounts of Pd_black-HSA
- b) Different batch of production of Pd_black-HSA;
- c) More mild degassing-baking temperatures;
- d) Higher D₂ pressure;
- e) Some unknown effect of due to the SS crucible.

During ICCF13 we heard of other experimental results, qualitatively similar, were obtained by other two groups: one in France (Prof. J.P. Biberian, Univ. of Marseilles, Ref. 8) and the other in Russian (Prof. V.A. Kirkinskii, Russian Academy of Sciences, Novosibirsk, Ref. 9).

They obtained, with Pd black, in some specific experimental conditions, clear evidence of anomalous excess heat.

Prof. Kirkinskii and Collaborators got excess heat also with a γ Al₂O₃-Pd compound, home made in their Institute.

Prof. Biberian got large amounts of excess power (about 5W, to be reconfirmed) at 80°C using small amount of material (100mg of Pd_black produced by Goodfellow, diameter of 80-180nm) filled inside a Pd tube (oxidised in air at 500°C). D₂ gas, pressurised at 9bar, was allowed to flux from the internal of the Pd tube to the external (buffer chamber) kept under high vacuum by pumping out.

It is worthy to note that, although gas loading of nano-materials allowed to obtain very good results from the point of view of reproducibility of the effects, from the other side, at least in our experiments, the amount of excess energy was quite low in comparison with the amount of material used (at the best, about 110mW/g). In previous experiments, using thin and long Pd wires by electrolytic methods, sometimes (but with poor reproducibility), we got some watt of excess power using only 20mg of Pd.

We think that the *flux* of Deuterium inside Palladium as to be induced: such flux was very large, at list in our experiments using thin wires, when electro-migration was applied to the wire. Something similar has to be done to the nano-materials. The experimental set-up of Prof. Biberian is a nice step to such direction.

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