Towards a High Temperature CMNS Reactor: Nano-Coated Pd Wires with D_2 at High Pressures.

F. Celani[1], P. Marini[2], V. di Stefano[2], M. Nakamura[2], O. M. Calamai[1], A. Spallone[1], E. Purchi[2], V. Andreassi[1], B. Ortenzi[1], E. Righi[1], G. Trenta[1], G. Cappuccio[1], D. Hampai[1], F. Piastra[1], A. Nuvoli[1]
(1) Istituto Nazionale di Fisica Nucleare, Laboratori Nazionali di Frascati, (INFN-LNF) 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 Tolomeo 1, 20010 Cornaredo (Mi)-Italy.
A. Mancini. *ORIM SpA, Via Concordia 65, 62100 Macerata-Italy*
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.*

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

Abstract. There were improved measurements on our reactor presented at ICCF14 (2008): long-thin Pd wires with surfaces nano-coated by multi-layers of several elements, D_2 at P<10bar; wires temp. <500°C; SS reactor wall temperature <100°C; longitudinal current density up to 45 kA/cm^2 (voltage drop up to 70V); transversal electric field up to 700V/cm. Previous ICCF14 results *confirmed:* anomalous excess power, stable over time and power cycling, up to 400 W/g of Pd. Made a new experiment with D_2-Ar mixture: demonstrated the role of high temperatures (into "nano" Pd-D) to enhance production of anomalous thermal effects. The combined effects of high concentration *and* mobility of D inside Pd seem the key points to get them: models based on ***High Temperature*** BEC Nuclear Fusion (Kim, Premuda) fits several of our experimental results. Experiments on the planned (new) High Pressure (60 bar) High Temperature (>600 °C) reactor wall are still in progress: experienced *heavy problems* coming out because degassing of impurities (specially S, P) from SS (304, 316) used in the reactor wall. The scavenger effect of H_2 (and D_2) on SS and other materials makes the impurities problem quite difficult to be overcome: designed and build a new, multiple layer wall (SS/Cu 3N), reactor that is now under the stage of final test.

1. Introduction

In the framework of experiments using Pd-based nano-materials and D_2 pressurised gas loading, we developed since 2004 an *hybrid* procedure that, in principle, takes advantage of several reproducible effects up to now introduced both from other Researchers and ourselves: Pd nano-particles, multi-layers, enhanced D diffusion (and D/Pd ratio) by flowing large current on thin Pd wires (with even transversal electric field up to 700V/cm). In short: high temperatures and D forced mobility through nano-Pd.
We recall that the Researcher that, in the field of Condensed Matter Nuclear Science, at first used concentrated Pd nano-particles to increase the D/Pd ratio was Prof. Yoshiaki Arata (Osaka University-Japan) since 1993 [1]; the first that developed multiple nano-layers of Pd-CaO was Dr. Yasuhiro Iwamura (Mitsubishi Heavy Industries, Yokohama-Japan) since 1999 [2]. Both used D_2 gas loading.
Our group applied (since 1995) the so-called *Preparata Effect* [3], to improve the D/Pd ratio on long and thin Pd wires by large voltage drop along the wire itself in electrolytic environments [4], i.e. with

maximum temperature <<100°C (cell not pressurised). In the experiment discussed in [4], was observed also the beneficial effect by coating thin layers of Ni, Li salts (the electrolyte), Pd to the main Pd wire due to side effects of both anodic corrosion of Ni (used as anode) and partial dissolution (and subsequent deposition) of Pd cathode itself due the specific pulsed operation (T_w= few μs) of the kind of electrolysis regime we developed (there was always present a little anodic component of the high power pulse, with voltage up to 200V and rise/fall time of less 100ns, due to inductive reasons). The main drawback of such procedure was that the kind of deposit and thickness was out of any control because both spontaneous and due to side effects (voltage undershoot) of pulses. Starting from 1999 we published several papers [5, 6] where was reported the beneficial effects of addition of soluble salts of alkaline heart elements (Ca, Sr, Ba), at very low concentration (10^{-4}M), in order to improve the D/Pd; moreover, the effect was magnified by several cathodic-anodic regimes: we observed (and published in 2003), by SEM, that Pd surface was similar to *fractals*. Later (2004) the effect to generate fractals was kept under better control by both deposition of proper elements (and subsequent heat treatments) before the use the Pd wire and using gaseous environments (P= 6bar) at wire temperatures of the order of 200-300°C. Since 2007 were made noticeable changing both to the procedure of preparation of the Pd wire and experimental set-up (Fig. 1, Fig. 2) in order to can operate up to about 500°C [7] and measure the Pd wire temperature/power emitted: by 2 similar wires (in Pt) one used as calibrator (Pt_cal) and the other as monitor (Pt_mon).
For a deeper understanding of our paper, because of length constrains of the Proceedings, we suggest reading: the ICCF14 paper [7], the ICCF15 oral presentation at:
http://iccf15.frascati.enea.it/ICCF15-PRESENTATIONS/S4_O3_Celani.pdf

2. Descriptions

We have made verifications, among others by instrumental improvements, of measurements previously presented at ICCF14 (2008, Washington D.C.-USA) on anomalous excess heat using thin (Φ=50μm) and long (l=65cm) Pd wires with surface covered by *several multi-layers of nano-materials* Pd included (nominally: Φ=6-9nm, S=300m^2/g; layers thickness <1μm). The excess heat was at macroscopic levels (up to 5W at the highest wire temperature operated of 500°C); the power density was 400W/g of bulk Pd or even larger (up to 5000-15000 W/g) if it is supposed that the main excess heat is generated between the several nano-layers. The current flowing inside the bulk Pd wire was up to 900mA, equivalent to a DC current density of 45 kA/cm^2. The contribution of nano-layers to the total electric conduction is just *supposed* to be negligible in respect to one of Pd bulk.
* We decided to modify further our previous preparation procedures (very shortly described also at ICCF14, [7]) of nano-coating proper (several) materials onto the Pd wire surface in order to make the nano-coated wire more "resistant" to aging effects due to several, *partial*, loading-deloading cycles.
* In addition, the material of the braid was changed from glassy fibres to pure quartz (in order to can increase wire's temperature, from about 520°C to 850°C): such changing, in principle, improves the thermal coupling between braids (thermal conductivity of pure SiO_2 is higher than mixed oxides of Si-Na-B glasses) but, at the same time, the overall thermal losses from the hot wires to the cold (30--60°C) internal wall of the reactor increase (wire temperatures are lower at the same electrical input power).
The main instrumental improvements were: a) addition of another long Pt thermometer surrounding all the previous 3-wires braid (the length of such Pt thermometer was 190 cm, i.e. about 3 times longer in respect to the (Pd-Pt-Pt) wires inserted into the braid); b) addition of others 2 thermocouples inside the pressurized SS chamber; c) external cooling (flow rate of 3-4 cc/s) water's bath (volume 15 l) temperature made more homogeneous by bubbling air inside it from the bottom. All the data acquired, after correction by calibrations using ^{4}He, were consistent each-others.
According to our measurement procedures, we made experiments in ^{4}He (calibrations, Fig. 3) and subsequently in D_2 (Fig. 4) gas atmospheres (both at 6.5 bar). Some crosscheck tests were performed also under vacuum conditions (P about 10^{-5}bar), pure Ar (.1-5.5bar), dry air (1-7bar).
We made new experiments also with a mixture of D_2--Ar (P=4.62--1.68bar; Fig. 5). The reason was to study if the effect of larger temperature of Pd wire, at same input power, could compensate for lower pressure of D_2 (6.5 → 4.6 bar) or even increase anomalous heat production. Thermal conductivity of Ar is over 7 times lower in respect to D_2 (T= 35--90°C): in the case of mixture D_2-Ar [8], adding 24% of Ar to pure D_2, the thermal conductivity is reduced (at 95°C) of 56% (from 151 to 96mW*m^{-1}*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 D_2 partial pressure reduction. Such important result pushed us to increase the efforts to overcome the technological problems of high temperatures: we get strong indications that, at least in our experimental conditions, the Pd-D_2 system has a "*positive feedback*"

behaviour from the point of view of anomalous heat generation with the increasing of Pd wire temperature. Moreover, after some temperature threshold value has been overcome (about 200°C in our experimental conditions), the energy gain slope looks *larger* than linear versus temperature increase.

3. Key characteristics of nano-coated Pd wires

The loading time to get a 0.8 D/Pd ratio (of the *bulk Pd*) at RT, using pressure of Hydrogen or Deuterium gas of 6.5bar, was of the order of 10-20 second. The gas addition time, from vacuum condition, was 4-5 s. The deloading time, using vacuum and high temperatures, 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 an almost "full" deloading. Anyway, we had indications that even such "heavy" procedures did not assure always a fully 100% Deuterium (or Hydrogen) out-gassing from Pd.
The whole effect was observed since 2002 even in electrolytic experiments: we named it the *DIODE EFFECT*. In other words, the good wires adsorb very easily the H_2 or D_2 and such gases, once absorbed, are very difficult to be desorbed.
In addition, we have some indications that the de-loading by direct heating of Pd wire (by Joule effect, and as a consequence some large voltage drop along the long Pd wire) is more difficult than of the deloading in indirect heating conditions (by the Pt_cal wire, near the Pd, used as heater, [6]). An innovatively speculative interpretation of such experimental behaviour is that the voltage drop along the Pd wire is operating against the D_2 deloading (possible experimental proof, of *Preparata Effect*).

4. Figure description.

The description of five figures are shortly reported as following:

Fig. 1. Photo of the three wires, each of Φ=50μm and l=65cm, before insertion in the SS reactor. Each wire (Pd, Pt, Pt) is inserted inside a quartz flexible sheath: they are closely braided each other. The braid is surrounded by several sheets of thermal insulating material (Superwool 607). It is high temperature annealed in air, before the use, to burn the several impregnating oils. Later it is vacuum degassed at 900°C. Similar treatments, at lower temperatures (700°C), are performed to the quartz sheaths.

Fig. 2. Photo of the whole experimental set-up with the SS pressurised reactor surrounded by water thank. The temperature of the water is kept stable by large cooling.

Fig. 3. Diagram of calibrations by ^4He (at 6.5bar). The wire temperature of Pd is lower (e.g. about 30°C at a Pt temperature of about 480°C) because the increased power dissipation ability of Pd surface due to the nanomaterials coated. Moreover, the apparent detected power is lower (over 1W at an input power of 75W) because nanomaterial effect. The temperature detected by the third Pt wire (Pt_mon.), used as monitor, is about 40% of the temperature emitted by the Pd or Pt_calibration wires.

Fig. 4. Typical experiment with pure D_2 gas at a pressure of 6.5bar at RT. There are shown the behaviours of R/Ro of Pd, versus the power applied, both for the power applied to Pd (orange line, direct heating of Pd) and to the Pt_cal wire (blue colour). It is noticeable the larger maximum value of R/Ro (e.g. 2.3) of Pd, with direct heating, in respect to the maximum value with indirect heating (e.g. 2.18). We stress that, in all of our experiments, the maximum value of R/Ro in direct heating condition is ***always*** larger in respect to the indirect one. Such behaviour, taking into consideration that the R/Ro is directly related to D/Pd ratio, can suggest that the large voltage drop along the Pd wire (the so called "*Preparata Effect*") due the current flowing inside the wire and/or the (new) transversal electric field toward the Pt wires (almost at zero potential) can be the reasons of such completely unexpected (and quite interesting) behaviour. Moreover, the energy gain increases at larger temperatures of Pd wires are due to both the combined effect of transition from β to α phase (larger diffusion coefficient, from $1.8*10^{-3}$ to about $4*10^{-3}$ cm^2/s) and larger temperatures itself (the diffusion speed increase largely increasing the temperature). Such combined effects overcome the reduction of D/Pd ratio (from about 0.8 to about 0.1) that, according to several Authors, will affect negatively the anomalous heat production in D/Pd systems.

Fig. 5. The experiment is like that described in Fig. 4 but with a gas mixture (D_2+Ar) optimised to increase, at the same input power, the wires temperatures. Because of larger temperatures, in spite of reduction of D_2 pressure (from 6.5 to down 4.64 bar), the energy gain increased of about 50% in comparison with pure D_2 experiments. Such behaviour, together with other observation in other our

experiments, suggested us that the *anomalous energy gain*, once overcome the threshold value (about 200°C in such experiments) has a *behaviour larger than linear increasing in Pd wire temperature.*

Fig. 6. Because of the evidence about the relative maximum of R/Ro may be important both for the understanding of the phenomenon of anomalous heat emission (in our experimental conditions) and even for basic studies (like ***High Temperature*** *Bose-Einstein Condensate*, see later), *after the Conference*, we assembled a new experimental set-up devoted to study deeper it and rule out the possibility of experimental artefacts. In short, the braid has been wrapped around a small diameter (6/4 mm) Cu tube with a thermocouple inside (called Tc_inA): we build a sort of furnace heated externally by the Pd or Pt_cal wires. In Fig. 6, apart the temperature measured inside the tube by the insulated thermocouple, it is shown (at high data acquisition rate of 1s) the behaviour of R/Ro of Pd when the power (i.e. under electromigration regime) is applied to Pd itself (R/Ro_max=2.33) or to the Pt_cal (R/Ro=2.28).

Fig. 1. - Photo of the 3 wires with thermal insulation.

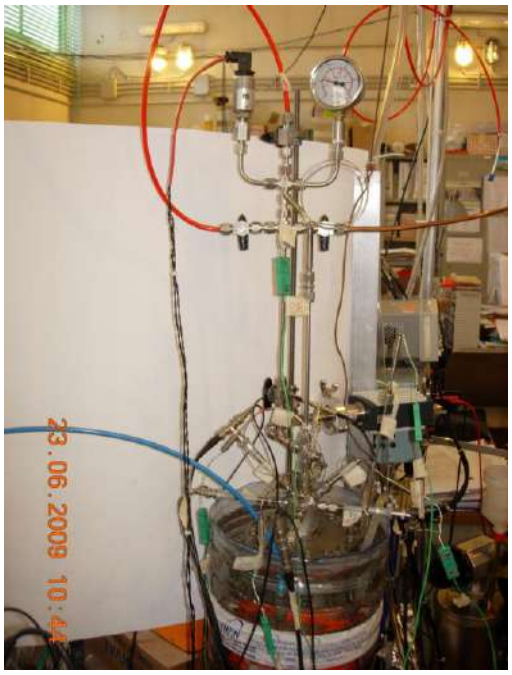

Fig. 2. - Photo of the experimental setup.

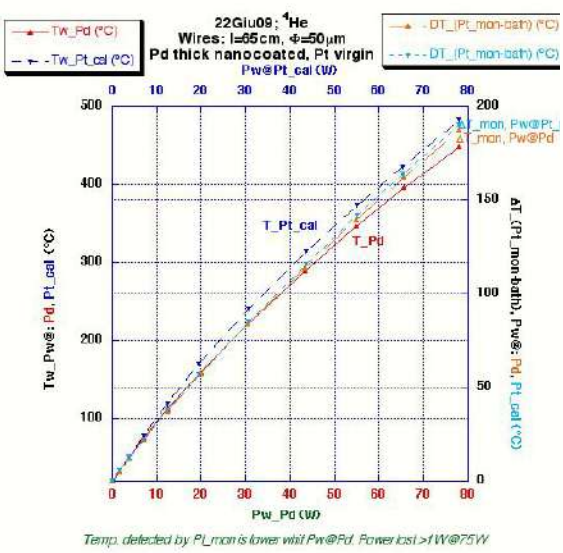

Fig. 3. - Calibration by ^{4}He.

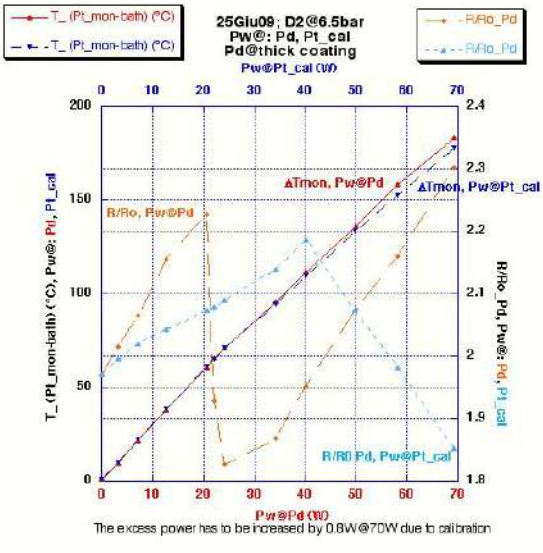

Fig. 4. - Experiment with D_2 pure at 6.5 bar.

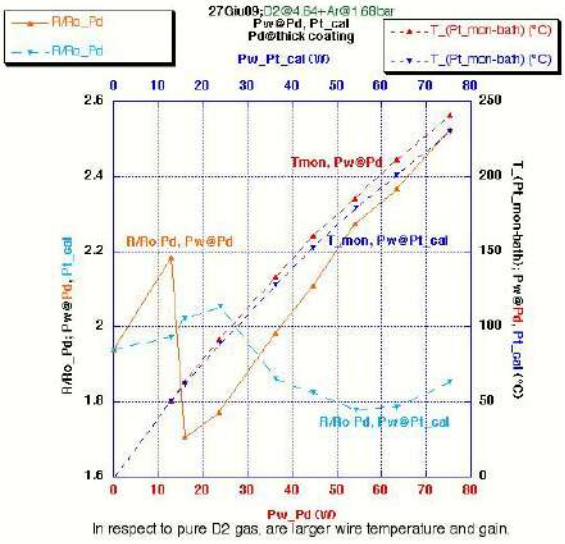

Fig. 5. - Experiment with D_2-Ar mixture.

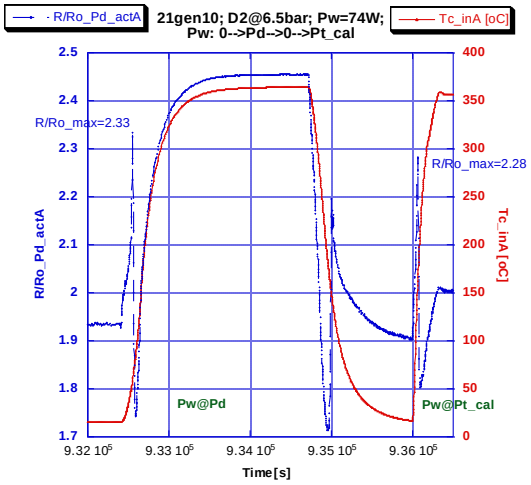

Fig.6. - R/Ro versus kind of power applied.

5. Conclusions

According to the experimental results we can argue that:

1) The data presented at ICCF14 were reconfirmed/reinforced (experiment with D_2+Ar mixture);
2) There are indications that increasing the temperature (e.g. the experiment with pure D_2 against the mixing D_2+Ar: at 70W of input power the Pt calibration temperature was 460°C in pure D_2 and 560°C in Ar+D2) and (probably) the pressure on nanocoated Pd wires can be possible to increase the gain. We hope that our improved (multi-layer: SS&Cu 3N) high temperature and pressure reactor (in construction) will allow to overcame the problem of "poisons" coming out from the reactor wall (at least, we identified the **S**, at 300-700 ppm concentration, that is always present in the typical SS AISI 304 and 316 used for pressurized vessel). The general problem of S was introduced in same details, in the CMNS experiments, by Tatsumi Hioki (and Collaborators) from Toyota Company [9] since 2007 during ICCF13 (Sochi, Russia).
3) The new specific nanocoating of Pd wires improved their overall stability against "aging" effects due to loading-deloading cycles (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 of CMNS reactions.*
5) Because there are several indications that the system, in our experimental operating conditions, can have behaviour of "positive feedback" versus the temperature, some efforts have to be done to find a procedure to keep the "reactor" under **full control**, specially at temperatures of 700-850°C were the theoretic Carnot efficiency is quite high (of the order of 70%). The Carnot efficiency is the quality factor for practical applications: conversion of heat to "noble" energy.
6) Y. E. Kim (Purdue Univ., USA) suggested that the experimental, fully reproducible, evidence of a R/Ro values of Pd larger with direct heating (i.e. power applied, or better to say current-voltage, to Pd wire) in respect to indirect one (e.g. Fig. 4, 5, 6), can be explained as a proof of *Bose-Einstein Condensation* in Pd-D system [10]. F. Premuda (Bologna Univ., Italy) introduced since 1993 the BEC as possible explanation of anomalies in D-Pd systems [11]. Our opinion is that such experimental evidence (if reproduced also in other Laboratories) is the result of several combined conditions: a) voltage drop (and/or large current flowing: e^-) along the long and thin Pd wire; b) large temperatures that reinforce the D flowing; c) effect of nanomaterials at the surface of the Pd wire (we experienced D/Pd ratio in nanomaterials even >1).
7) More work is needed both to increase the anomalous heat generation and identify the nuclear channels of the reaction (e.g. ^{4}He, transmutations, isotope changing,…).

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* As quoted in the introduction, our work was also "inspired" by the experiments with nano-Pd (up to the recent $Pd_{35}Zr_{65}$ and Zr_{65}-Ni_{30}-Pd_5) absorbing Deuterium, as pioneered by Academician Yoshiaki **Arata** (Osaka University, Japan). Replication experiments (with $Pd_{35}Zr_{65}$ produced by Santoku Company at Kobe tanks to joint collaboration University-Industry), performed by Akito **Takahashi**-Akira **Kitamura** group (respectively at Technova Inc.,Tokyo and Kobe University, Japan), reinforced both the Y. Arata results and our decision to pursue the nano-material "route" [12]. The pioneering work on multi-layer Pd-CaO, performed by Yasuhiro **Iwamura** group (at MHI, Yokohama, Japan), give some hints to develop our simplified "Atomic Layer Deposition" process made by chemical-thermal-mechanical procedures. Obviously, the system operated in tunneling regimes because of small dimensionality and the expertise/comments of Nobel Laureate Brian **Josephson** were important for us. The experiments performed independently by Prof. **Li** Xing Zhong (Tshingua University, China; from 2002) and Jan Paul **Biberian** (Marseille University, France; from 2006) using Pd tubes (with even surface oxidized) reconfirmed the importance of surfaces/nanomaterials to promote anomalous thermal effects, although not stable versus time (surface damaged by the reaction itself). In deep discussions with the previous Scientist helped us to avoid mistakes and optimize our operations: we are deeply indebted with them.

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