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Toward the use of nanoparticles for stable excess heat in Pd-D system: progress report at INFN-LNF

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INTRODUCTION

*** Since 2003, we suspected and later get evidence that nanostructures (or fractals) at the surface of Pd make a key role in obtaining anomalous effects in Pd-D system, both of nuclear (like transmutations) and/or thermal origin.**

*** We presented several papers, at JCF, Asti and ICCF Conferences which aim was to explore the role of nanometric Palladium. *We developed a (complex) procedure to oxidise-produce fractals/holes at Pd wire surface, during electrolysis*.**

*** Up to April 2006 we studied mainly thin (50μm) and long (60-100cm) Pd wires, both in electrolytic and gaseous environments.**

*** We developed a new type of colloidal silica, nanometric size (3nm), that was "painted" on the thin Pd wire or added to our specific electrolytes solutions (C_2H_5OD 90%, D_2O 10%; salts of Th, Hg, Sr at micromolar concentration).**

NEW APPROACH

Following the very interesting experimental results shown by Yoshiaki Arata (Osaka University) at ICCF12 (November 2005, Yokohama), about very large (over 10 °C) temperature "gain" at high temperature (180°C) in a nano-particles (ZrO_2-Pd) Deuterium gas system, we tried to produce similar results using Pd with "our" colloidal silica. Moreover, some tests were made using commercial Pd-black.

We anticipate that, very recently, Prof. Arata got a temperature gain as large as 40 °C, at a remarkable temperature of 210 °C.

LNF Experimental activity

In order to develop the fabrication procedure with powders we made the following steps:

a) **Studies, as references, on the gas loading of the wires (just cleaned and stress released; oxidised; oxidised and colloidal silica painted) using a Sievert apparatus (moles of D_2 absorbed) at NTP. Experiments performed at INFN-Univ. Perugia. Comparison with Baranowsky curve.**

b) **Production (home made) of micro-granules (diameter 10-100μm, length 0.5-1mm) of Pd. Oxidation by air in quartz furnace at 750 °C; reduction by fast cooling from 800°C. Further characterization of oxygen intake by TGA and TDA (CSM, Castel Romano, Italy). Composition by XRPD (INFN-LNF). Size by optical microscope.**

c) **Production of new compounds by heating at 750 °C the micro-granules with colloidal silica. Analysis by XRPD and SEM (CSM).**

d) **Studies of Hydrogen, Deuterium absorption by a new "multifunction" Sievert apparatus (HPT reactor #1, SS reaction chamber with a length of 40cm and internal diameter 10mm), build at LNF, that can operate also as a thermal reactor (14W Joule heater installed), between: 77 to 630 K, vacuum to 200 bar.**

Heat losses: 4W at ~ 140 °C; 6W at ~ 190°C; 12 W at ~ 300°C.

e) **Studies of particle sizes by proper mixing Pd-black and colloidal silica. The compound underwent proper high temperature cycles. Analysis by XRPD, SEM, HPT reactor (thermal anomalies, if any).**

f) **Studies, by HPT reactor, of Pd-black from the point of view of H, D absorption and some thermal anomaly. Measurement, before and after Deuterium absorption, of particle dimensions by SEM.**

g) **Work in progress……**

Experimental Procedures

*** The wire, before painting, underwent proper several high temperature cycles (by Joule heating) in order to get a fractal surface due to oxidations→ reductions→thermal quenching of Pd surface.**

As shown in Fig. 1[1], a very interesting property of Pd is the relationship between the Temperature and the Oxidation state. In fact, during the heating cycle, a growing Oxidation state (PdO) can be observed from ~ 700 K to a critical temperature T_d, which depends on partial Oxygen pressure as shown in Fig. 2[1].

When temperature is larger than critical value Td, a very fast reduction is observed. Carrying back temperature to ~ 700 K, if the process is controlled and not too fast, a new Oxidation can be observed, following the same curve of Fig. 1 to the opposite direction. Moreover, if a very fast cooling (quenching to room temperature) is performed, the oxidation can be strongly reduced.

Making a lot of cycles, fractals on surface could be created, according to our conjecture.

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[1] Journal of Phase Equilibria Vol. 23 No. 3 pag. 246-248 (2002)

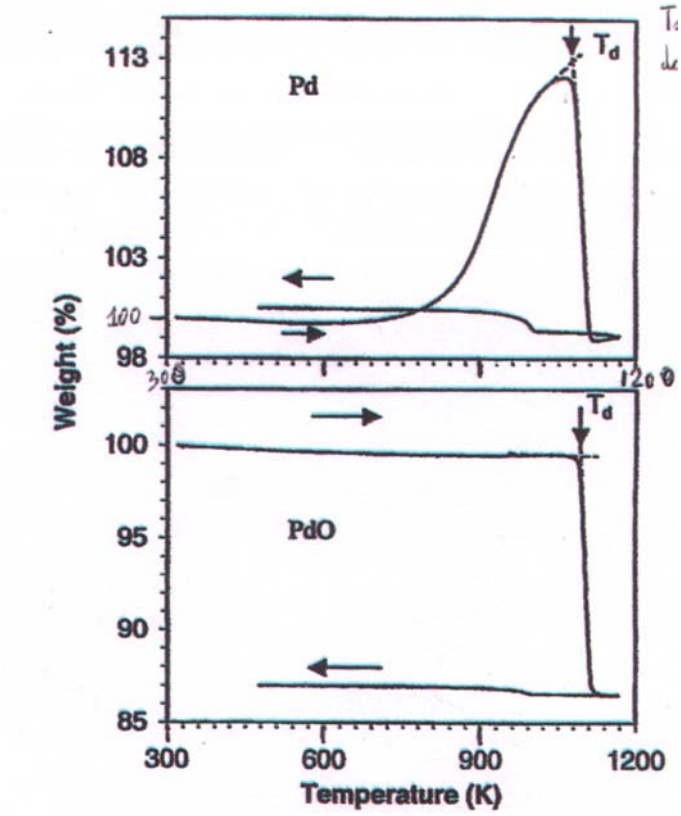

Fig. 1 TGA results for the Pd and PdO samples under air using a scan rate of 20 K/min (right arrows indicate heating directions and left arrows indicate cooling direction).

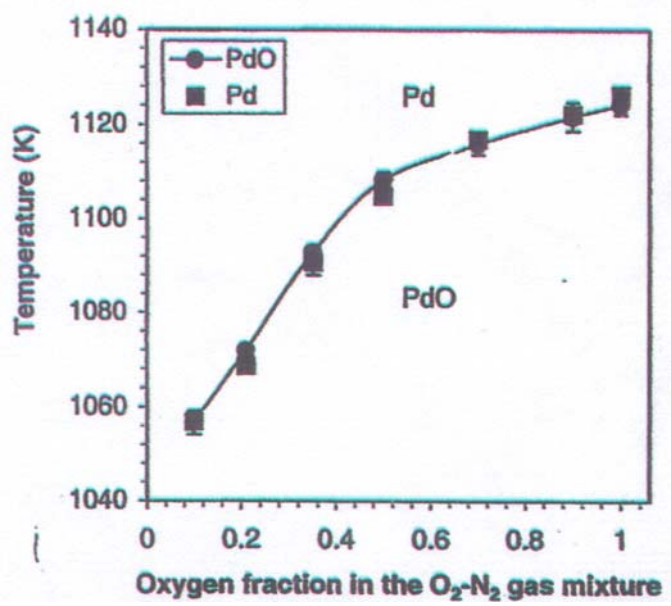

Fig. 2 Decomposition Temperature of PdO against oxygen partial pressure in oxygen and nitrogen total pressure of 1 atm for the PdO and Pd powder samples.

After such thermal treatments, the colloidal silica was gently painted (or immersed in a proper glass) on Pd wire surface and again the Pd wire got others proper high temperature cycles in order to stabilise the new "compound" obtained (like Palladium silicate and/or Palladium – Silica glass.

*** The results, about speed of Hydrogen/Deuterium Loading, and the maximum value of D/Pd ratio (measured by the R/Ro value, the so called "Baranowsky curve") both in electrolytic (Fig. 3) and gaseous environment (Fig. 4-5), were really "good" as shown in the following graphics.**

Fig. 3 shows experimental results of H/Pd ratio for Pd/PdO/PdO+Colloidal Silica in electrolyte environment. The loading speed is extremely large (less than 100 sec to get a R/Ro value from 1 to 1.9).

The maximum value of R/Ro is 1.9 instead of 1.8 due to effect of stress induced by H absorption.

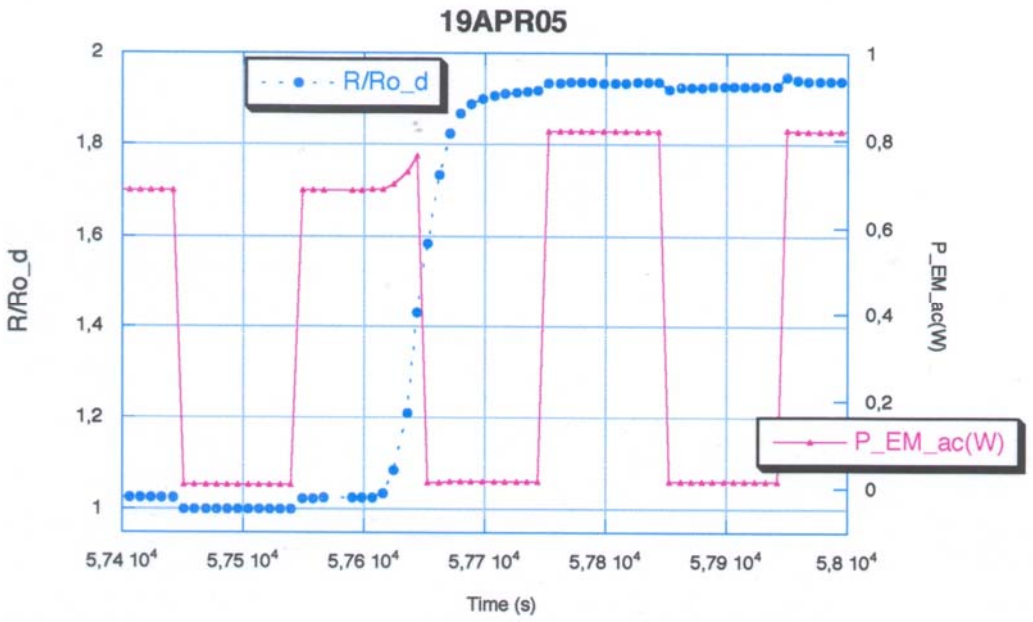

Fig. 3[(2)] As standard in our procedure from about 2 years, we cyclically inject electromigration current (square wave, 10 KHz) with low (about 10-15 mW) and high power (700-800 mW) in order to calculate the Resistive Thermal Coefficient versus D/Pd ratio. This graphic shows the behaviour of R/Ro and AC power in the wire oxidised and painted by colloidal Silica. The time to reach R/Ro=1.90, from the beginning of experiment, was less than 100 seconds.

(2) Presented at ICCF12, Yokohama November 28 – December 4, 2005

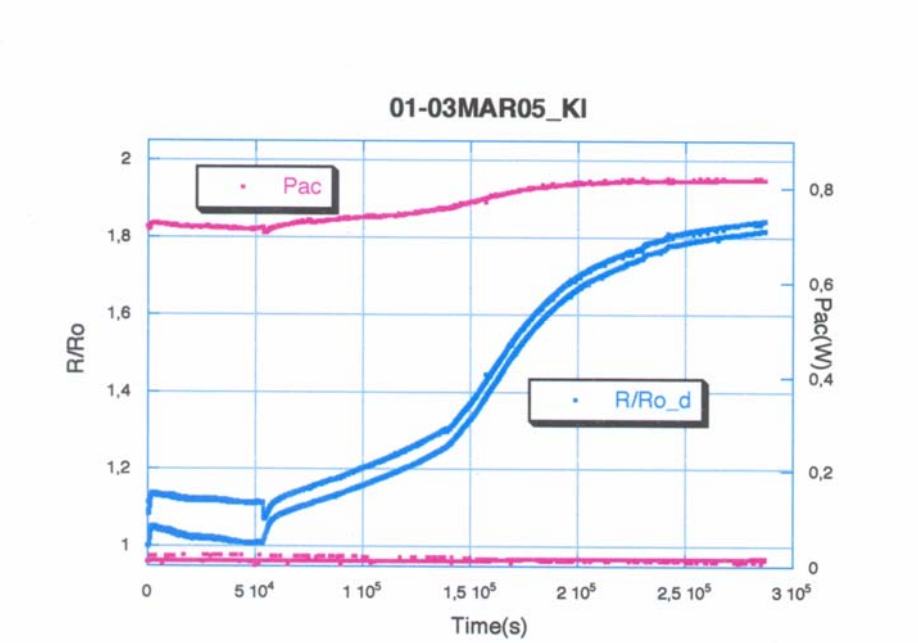

Fig. 4[3] Loading characteristic of a virgin Palladium wire loaded at room temperature with 1 bar of deuterium gas. In order to "activate" the Pd surface, it was made a preloading cycle (from time 0 to 60000s) with D_2 gas, 293 K, 1 bar and later allowed to decrease, very slowly, the Deuterium content in the cell. Even neglecting the activation time, the time needed to reach the thermodynamic limit of R/Ro=1.82 is as large as 220000s. Such values (i.e. R/Ro and time) are in agreement with data usually reported in literature. Wire, before use, was cleaned according to the procedure: Acetone→Water→HNO_3 65%, 3^{min}→Water

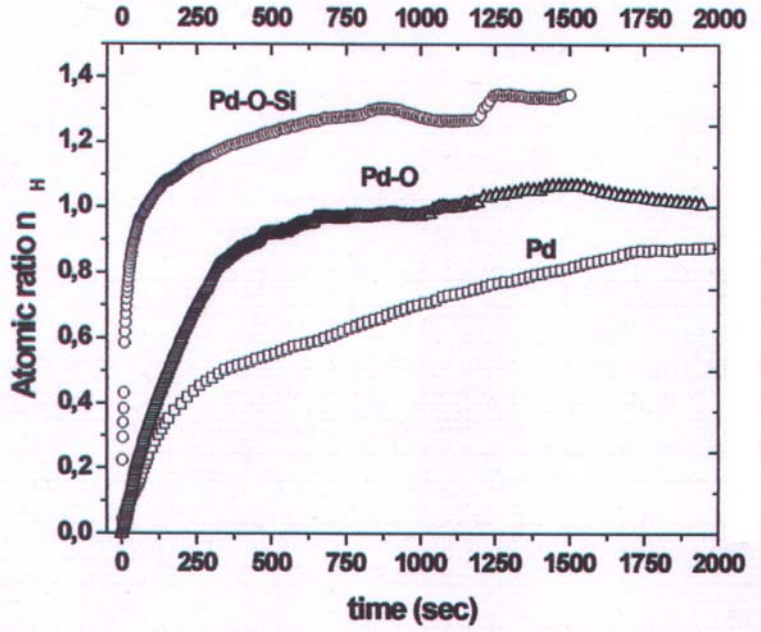

Fig. 5[4] H/Pd ratio, at T=22°C, 1 bar pressure, for thin wires (ø=50 μm, l=100cm, weight 22mg) of a) pure Pd heated in air at about 450 °C; b) PdO at ~ 700°C, c) PdO, oxidized at high temperature, treated with many heating cycles of heating at high temperature and quenching, and for each cycle painted with nanometric colloidal silica 3-5nm (cycles PdO→Pd→PdO). All the 3 Wires, before use, were cleaned according to the procedure: Acetone→Water→HNO_3 65%, 3^{min}→Water.

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[3] Presented at ICCF12, Yokohama November 28 – December 4, 2005, Publishing by World Scientific 2006.
[4] Presented at Italian Physical Society Annual Meeting, Turin - September 18-23, 2006.

*** Moreover, several times were detected specific new elements that depend on the kind of salt added to the electrolyte (e.g. Sr→Mo, Th→Hg, almost always detected Cu and Zn). In some aspects, the results were similar to what found by Yasuhiro Iwamura (Mitsubishi Heavy Industries, Yokohama, Japan) that used nanometric multilayer of Pd/CaO/Pd structures in gaseous Deuterium. These results are shown in the following Figures.**

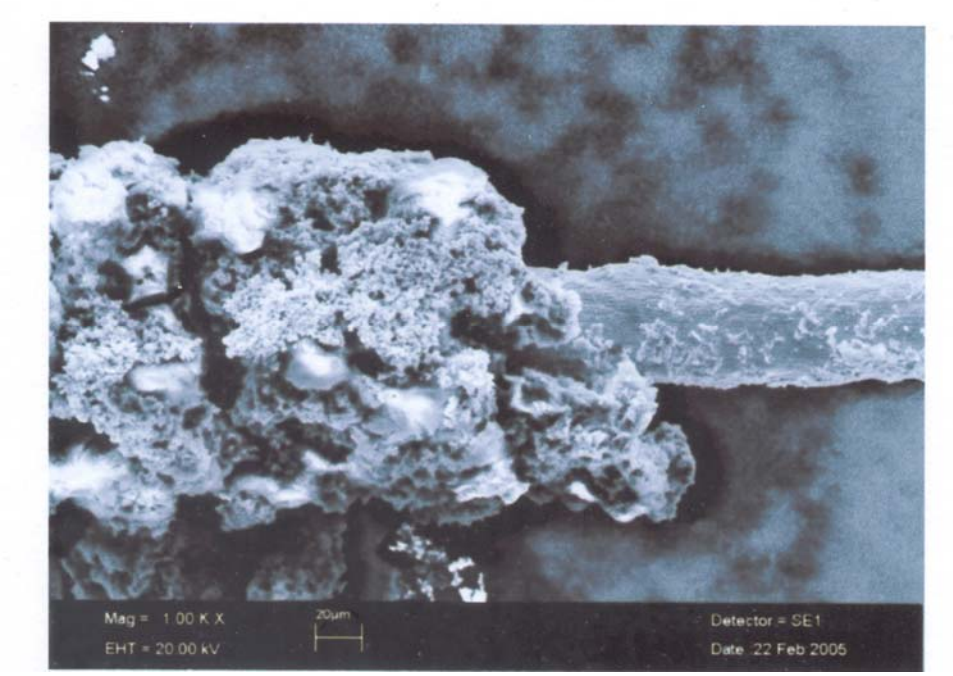

Fig. 6 Details of Pd wire after Anodic-Cathodic electrolysis. By SEM, it is visible the fractal surface and deposits of salts

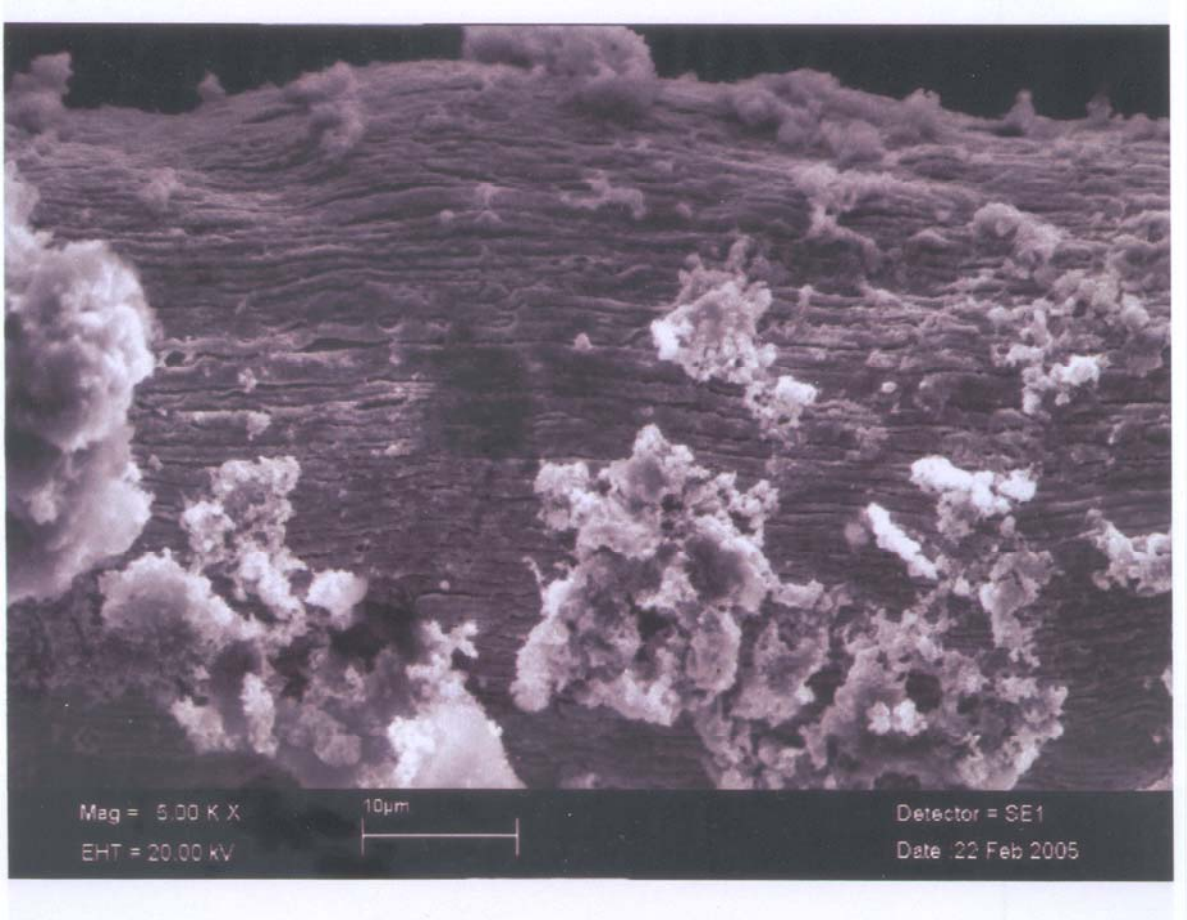

Fig. 7 Other details of the wire shown in Fig.6

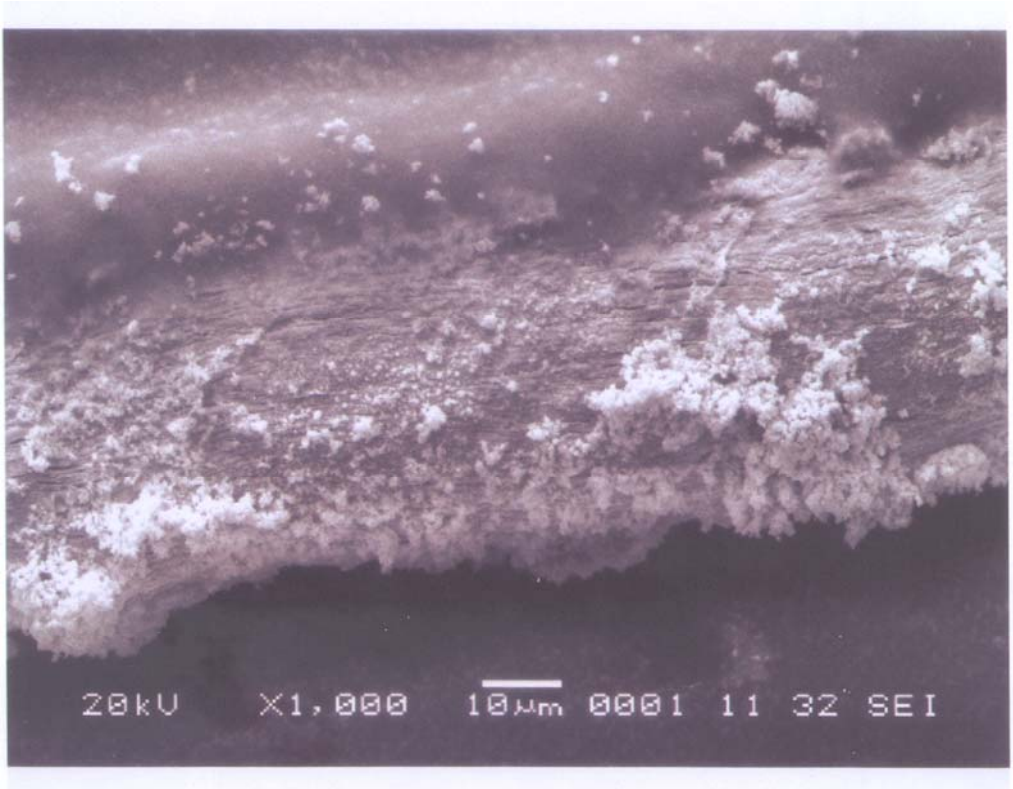

Fig. 8 Other details of the wire shown in Fig.6

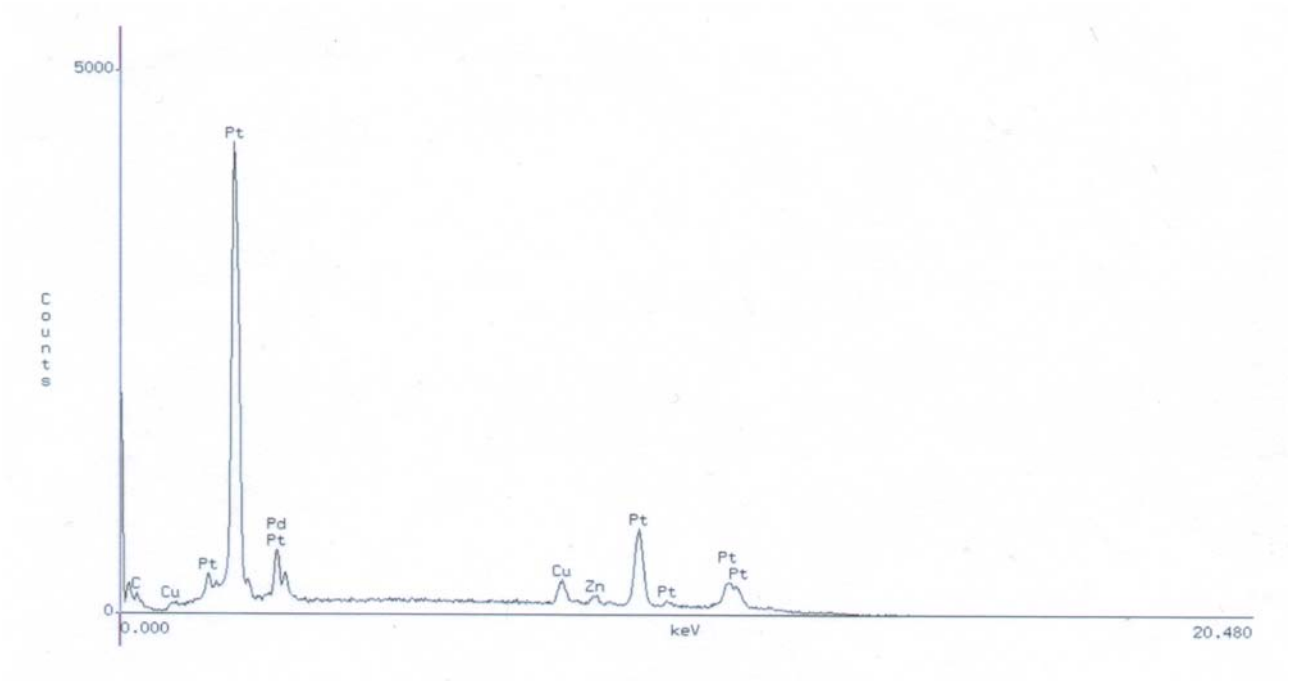

Fig. 9 SEM elemental analysis of one of "white" area as shown in Fig.5. The, unwanted, large deposition of Pt at Pd surface is clearly detected. Moreover, also Zn and Cu, detected by ICP-MS analysis, are reconfirmed.

Since in a lot of cases new elements has been detected, two experiments were made to remove doubts concerning contaminations: the first using light ethyl alcohol-water (C_2H_5OH 90%, H_2O 10%) as electrolyte, the second using heavy ethyl alcohol-water (C_2H_5OD 90%, D_2O 10%).

The interesting result is that, when heavy solution was used, the new elements were detected in larger amount as shown in the following Tab. 1.

ICP-MS Results

(1 Count = about 5E10Atoms)

Main new elements detected in light alcohol-water (Pyrex type) and heavy alcohol-water (quartz) cell; reagents heavy. BKG and reagents subtracted.

Type Element	Light Exp.	Heavy Exp.	Comments
P	0	6.4E6	BKG=4E3
^{39}K	0	1.8E7	BKG=1E6
Cu	2.3E6 63/65=2.20	2.5E7 63/65=2.11	63/65 Nat.=2.25
Zn	6.2E6	4.9E7	
Rb	3.1E4	8.2E4	
^{108}Pd (26.5%)	Normal	Depleted of 5%	
Ag	6.5E4	2.6E5	
^{140}Ce(88.5%)	1.86E4	1.31E5	
W	1.16E4	4.42E4	
Tl	80	900	
Pb	**4.5E5**	**1.38E7**	
U	1.1E3	1.0E4	
^{195}Pt(33.8%)	4.3E7	10.8E7	Mark. anode diss.

Tab.1

Pd Needles

Pursuant to the thin-wire studies, we began to study properties of Pd needles.

First, we heated Pd needle for 25 min at 700°C and then we heated it for 50 min at 800°C, as shown in Fig.10 and Fig.11.

According to Fig. 1 and Fig. 2, a peak of PdO can be observed for T< limit temperature T_L, then a reduction is observed.

Fig. 12 shows thermogravimetry on Pd needle.

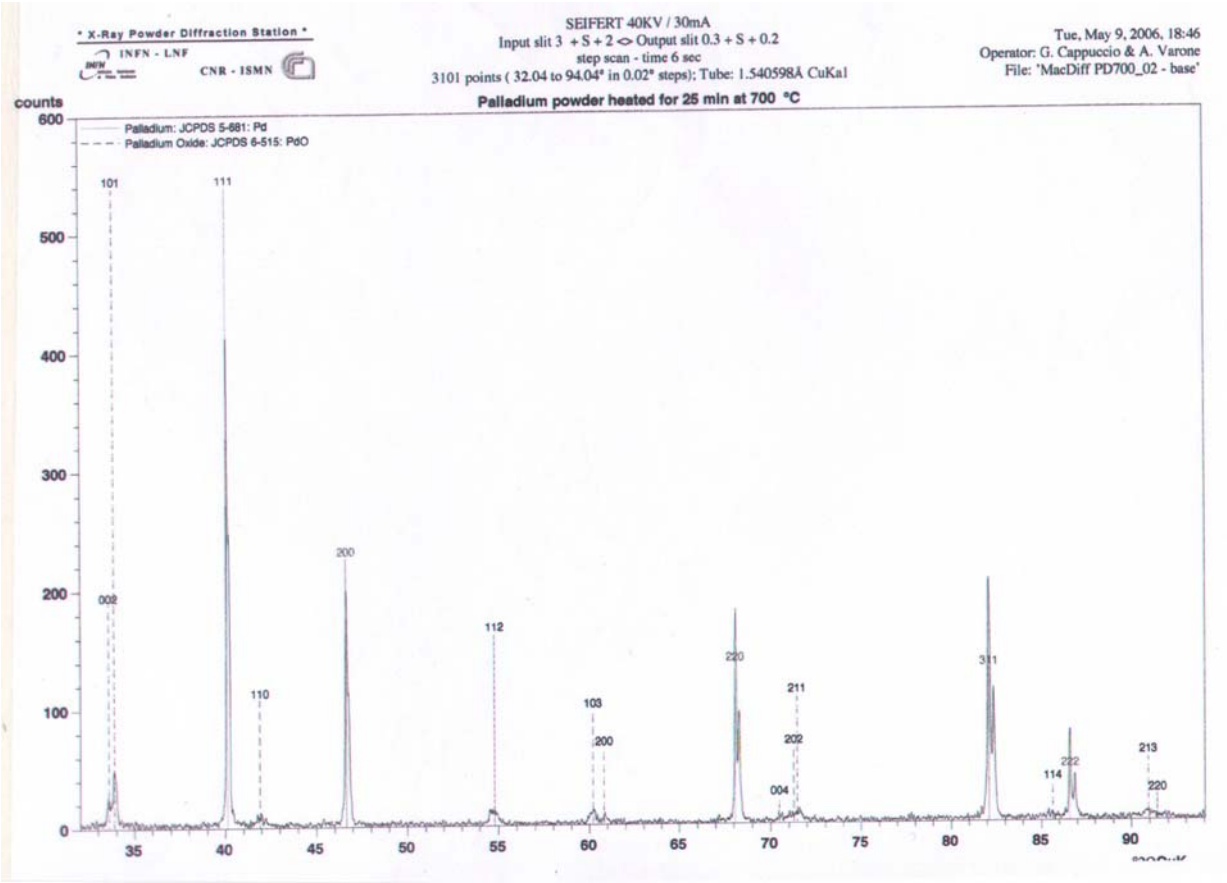

Fig. 10 Palladium powder heated for 25 min at 700°C by furnace tube in quartz crucible and tube (XRPD plot).

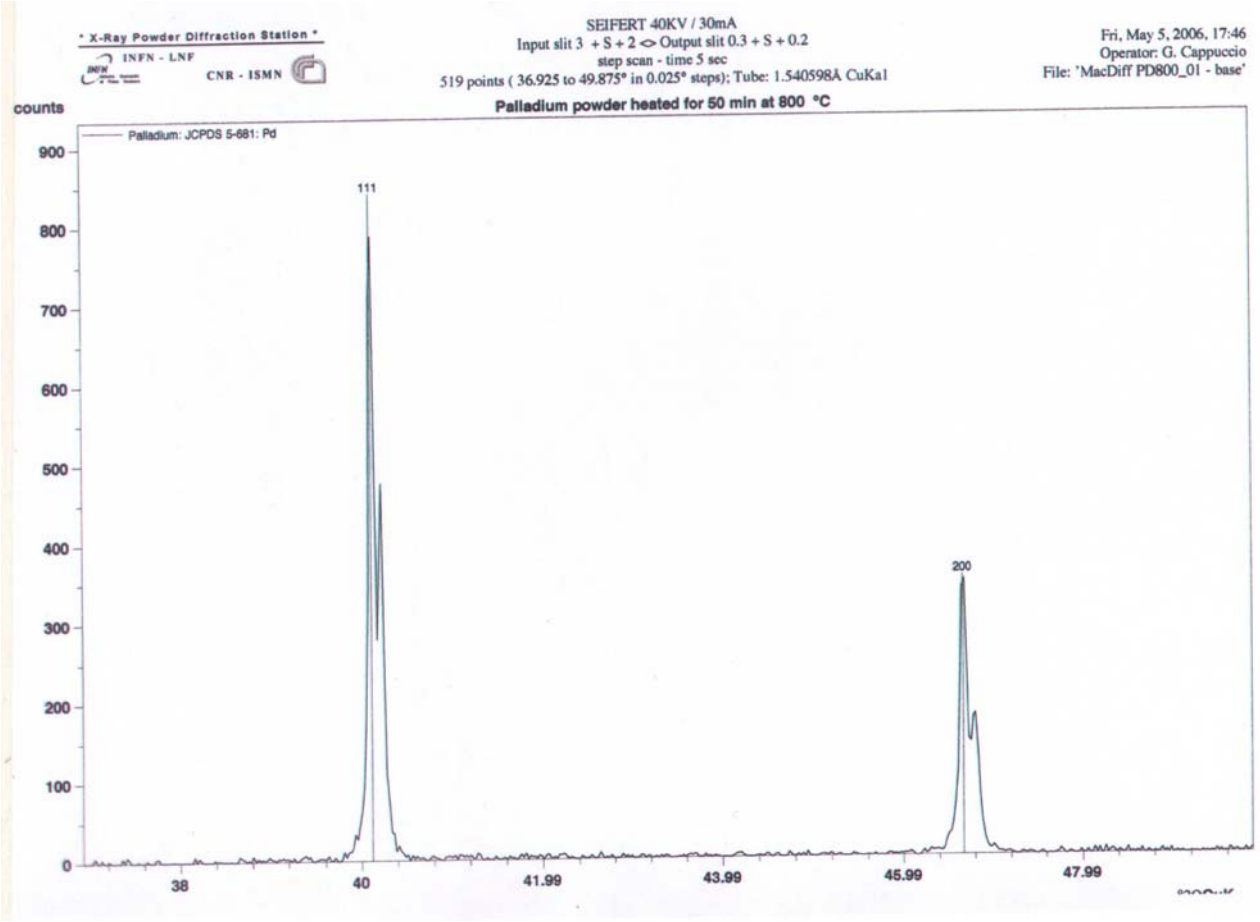

Fig. 11 Palladium powder heated for 50 min at 800°C (XRPD Plot)

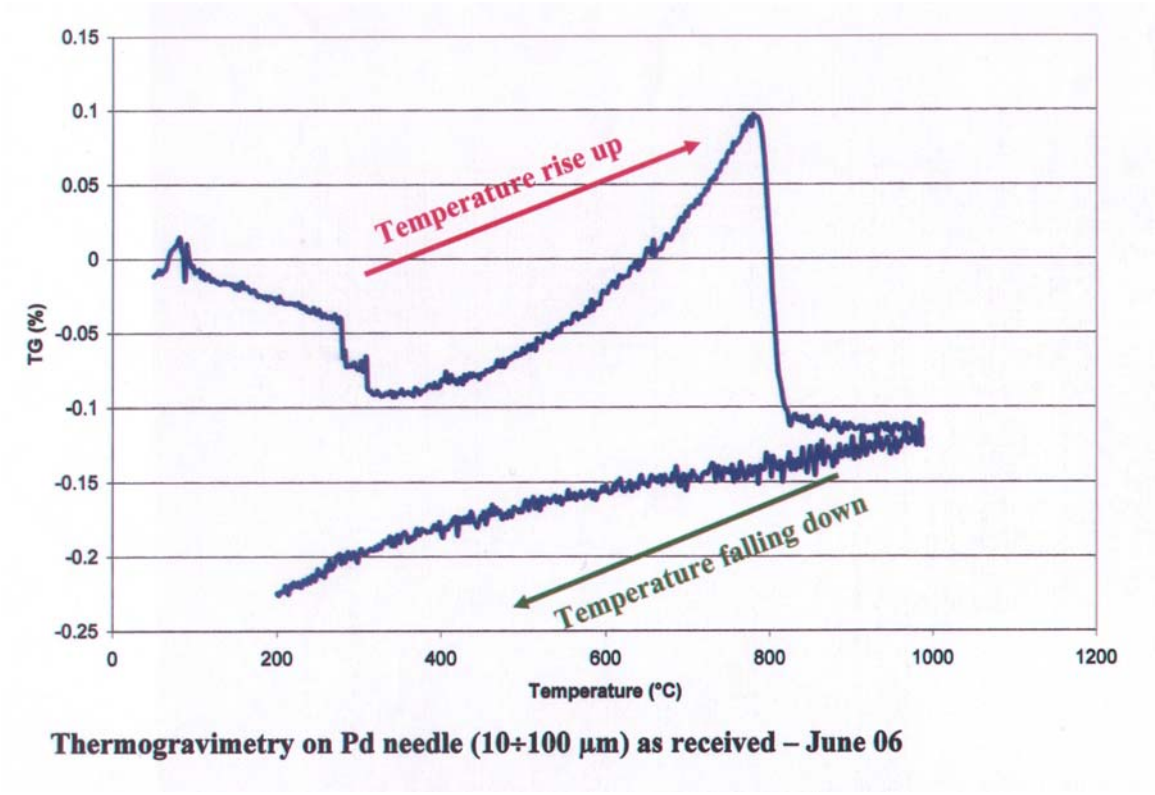

Fig. 12 Thermogravimetry on Pd needle. The abrupt loss weight at 800°C is observed, confirming the reaction PdO→Pd

Afterwards, we "mixed" Colloidal Silica with Pd needle and even with Pd black, trying to make the amorphous Silica on the Pd surface after proper thermal treatments. In fact, as shown in Fig. 13 (Pd Black+Colloidal Silica), we detected no crystalline Silica, but only amorphous Silica.

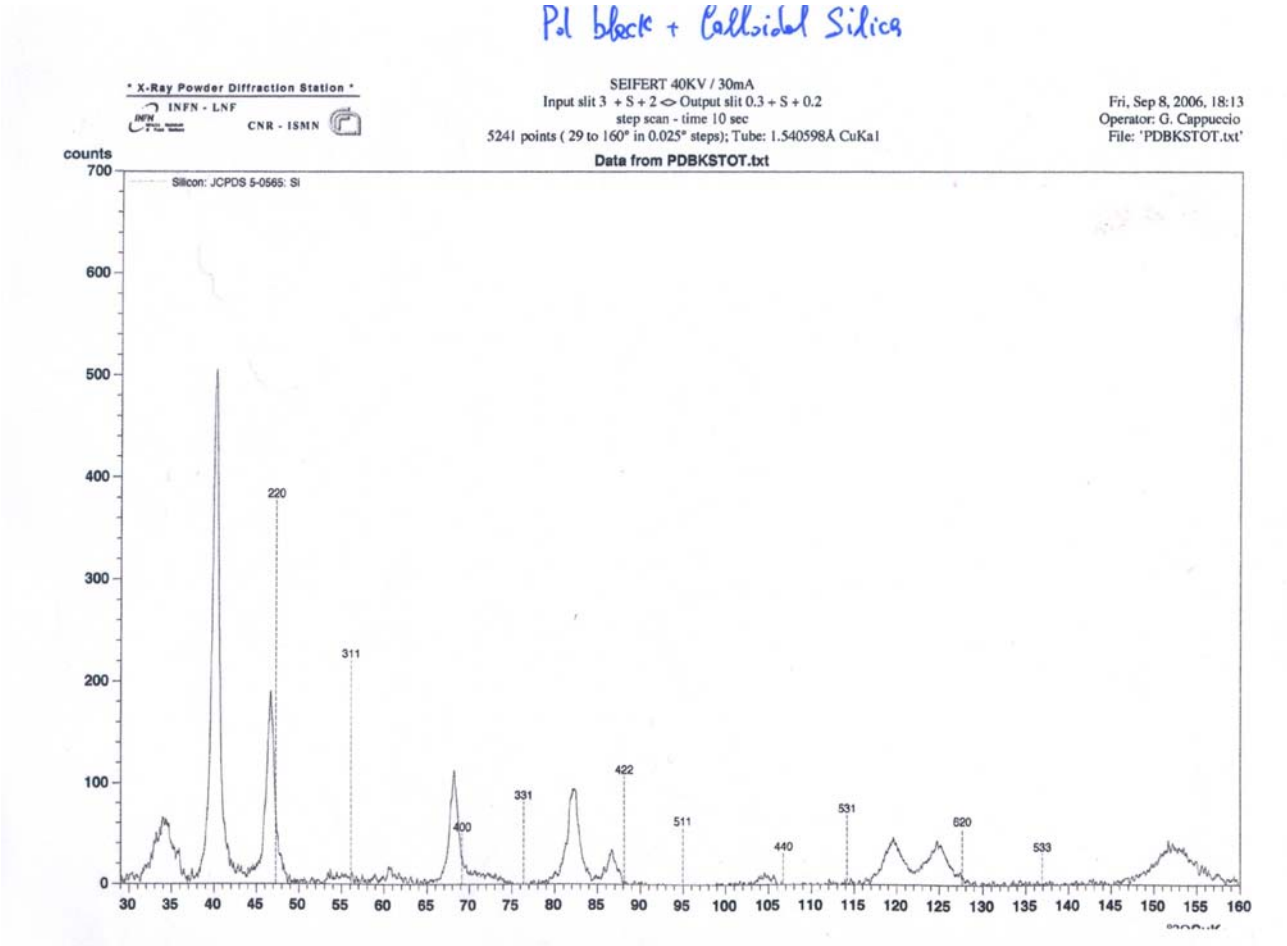

Fig. 13 Pd Needle+Colloidal Silica: no crystalline Silica detected

The following Figures show the set up of our experiments with high pressure and temperature gas (HPT chamber):

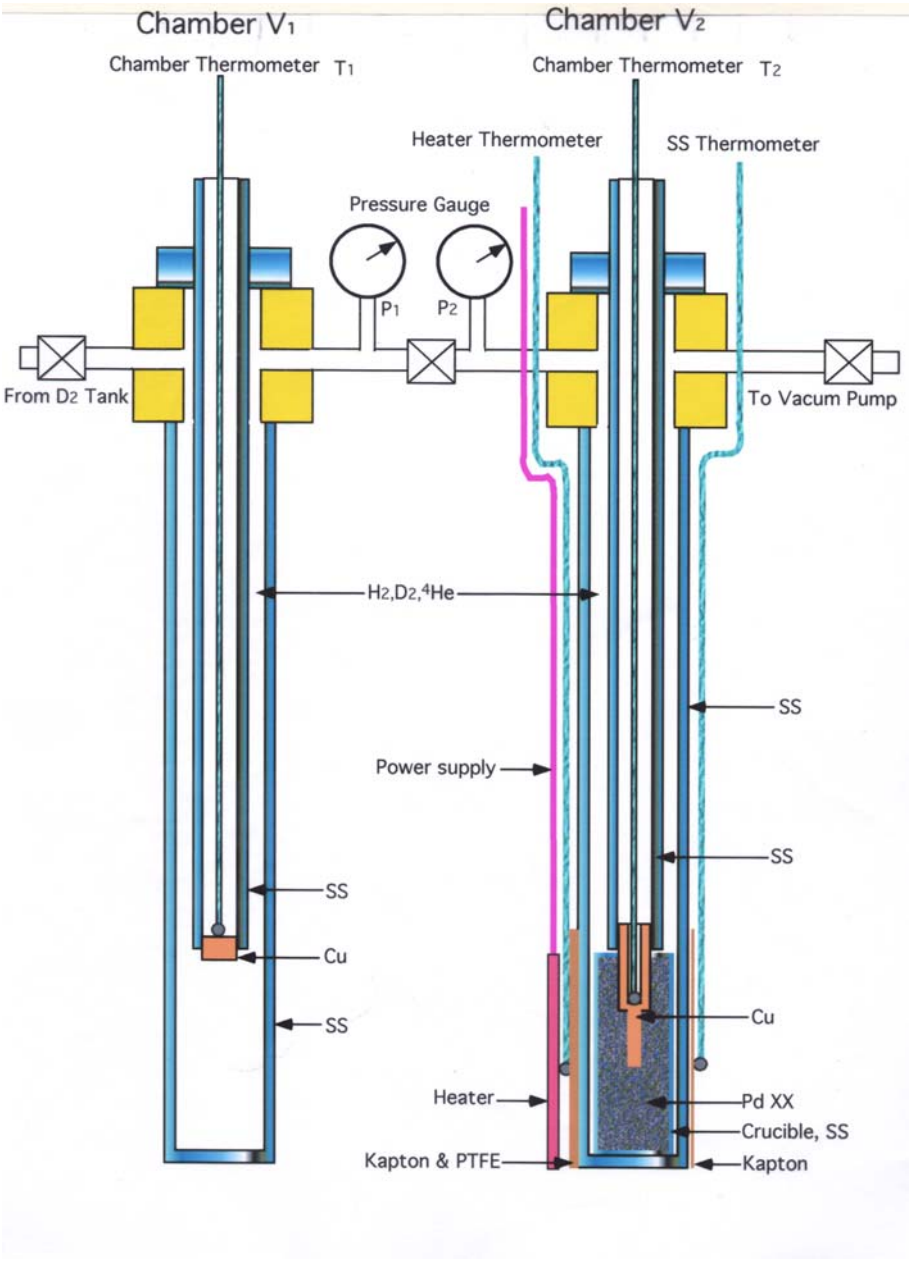

Fig. 14 Chambers of our experiments. V1 is the reference chamber, where the H_2, D_2, N_1 moles are stored.

$N_1 = \frac{P_1 \cdot V_1}{R \cdot T_1}$ **with R (gas molar constant) equal to 8.314 J mol^{-1} K^{-1}.**

In V1 only the T1 chamber temperature is measured.

V2 is the reaction chamber, provided of heater and, a part T2 chamber thermometer, 2 extra thermometer are used: on SS wall and on heater.

The absorption of H_2, D_2 in the PdXX sample is calculated by mass loss procedure:

Phase 1: V1 filled with N1 moles of H_2, D_2, ^{4}He, Ar

V2 vacuum

Phase 2: V1 and V2 are connected.

At equilibrium: $N_F = \frac{P_F \cdot (V_1 + V_2)}{R \cdot \left(\frac{T_1 + T_2}{2}\right)}$.

If there is absorption N1>N_F , calling ΔN=N1-N_F; considering the moles of Pd involved (weight in g/106.4, where 106.4 is the molecular weight of Pd), we get:

H,D/Pd=2 ΔN/Pd.

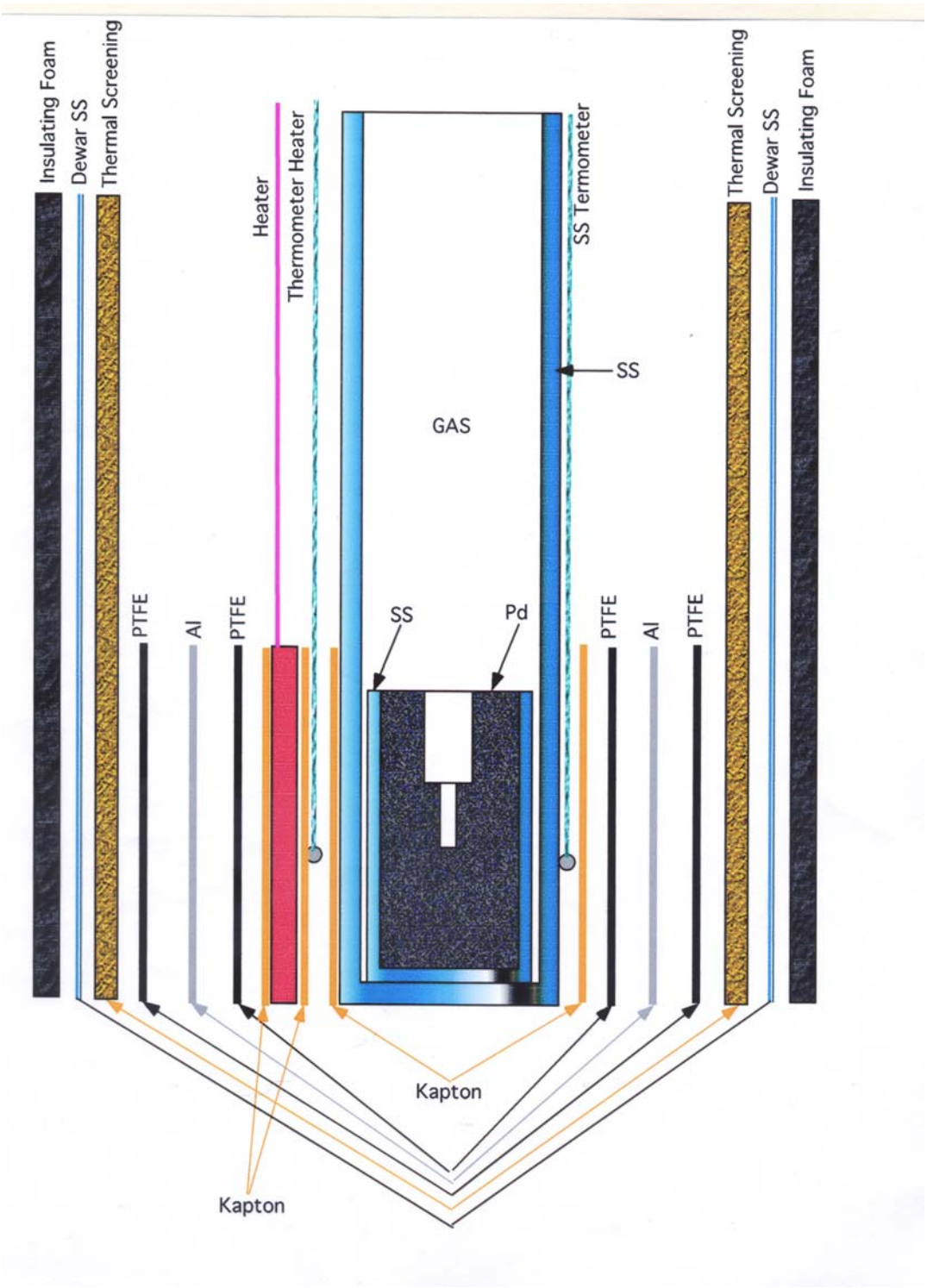

Fig. 15 Detail of Fig. 14: Reaction chamber V2

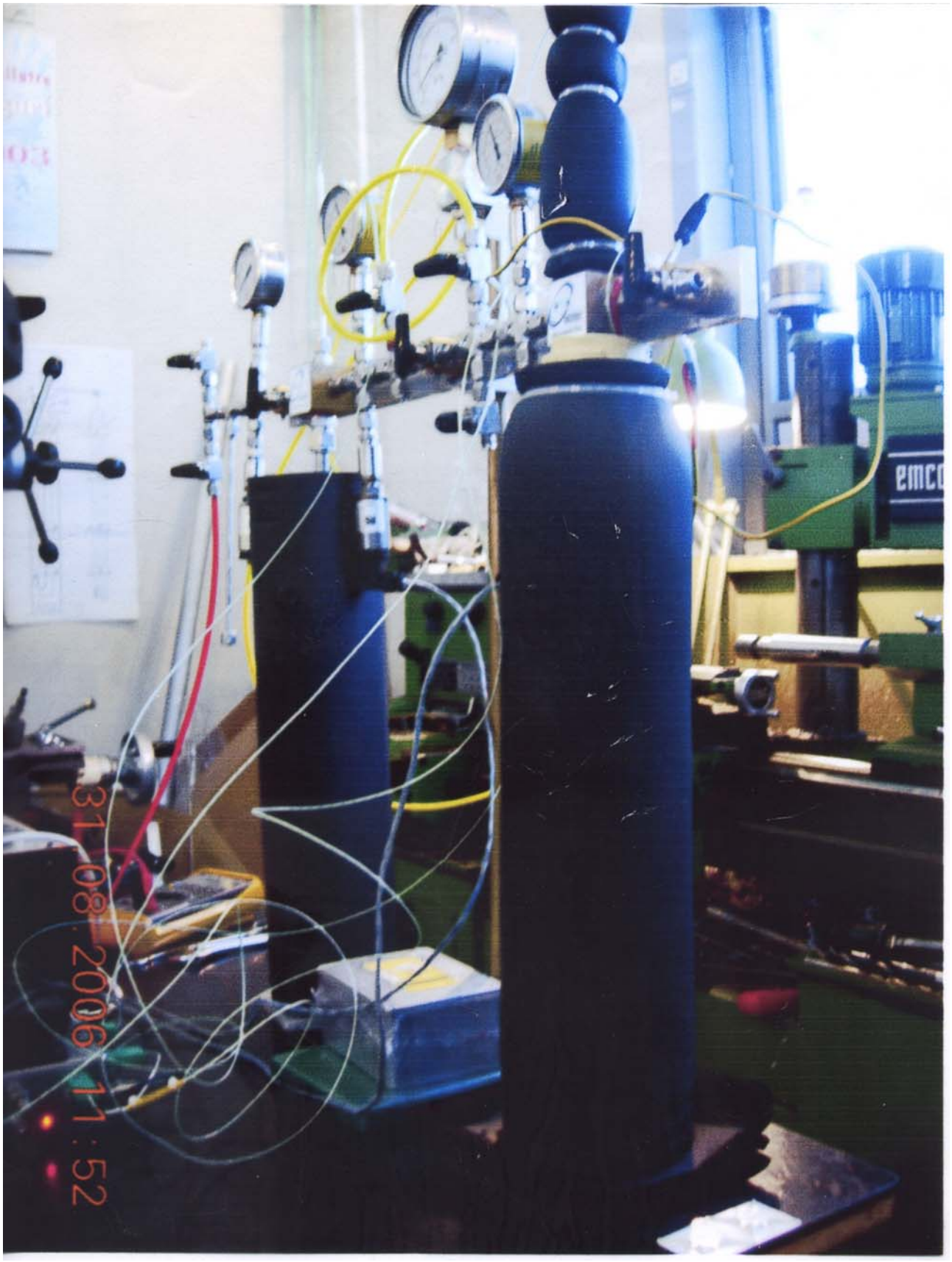

Fig. 16 Experimental set up with the two chambers, pressure gauges (both high resolution electronics (0.25% FS) and analogical mechanical manometer) and thermometers (thermocouples type K).

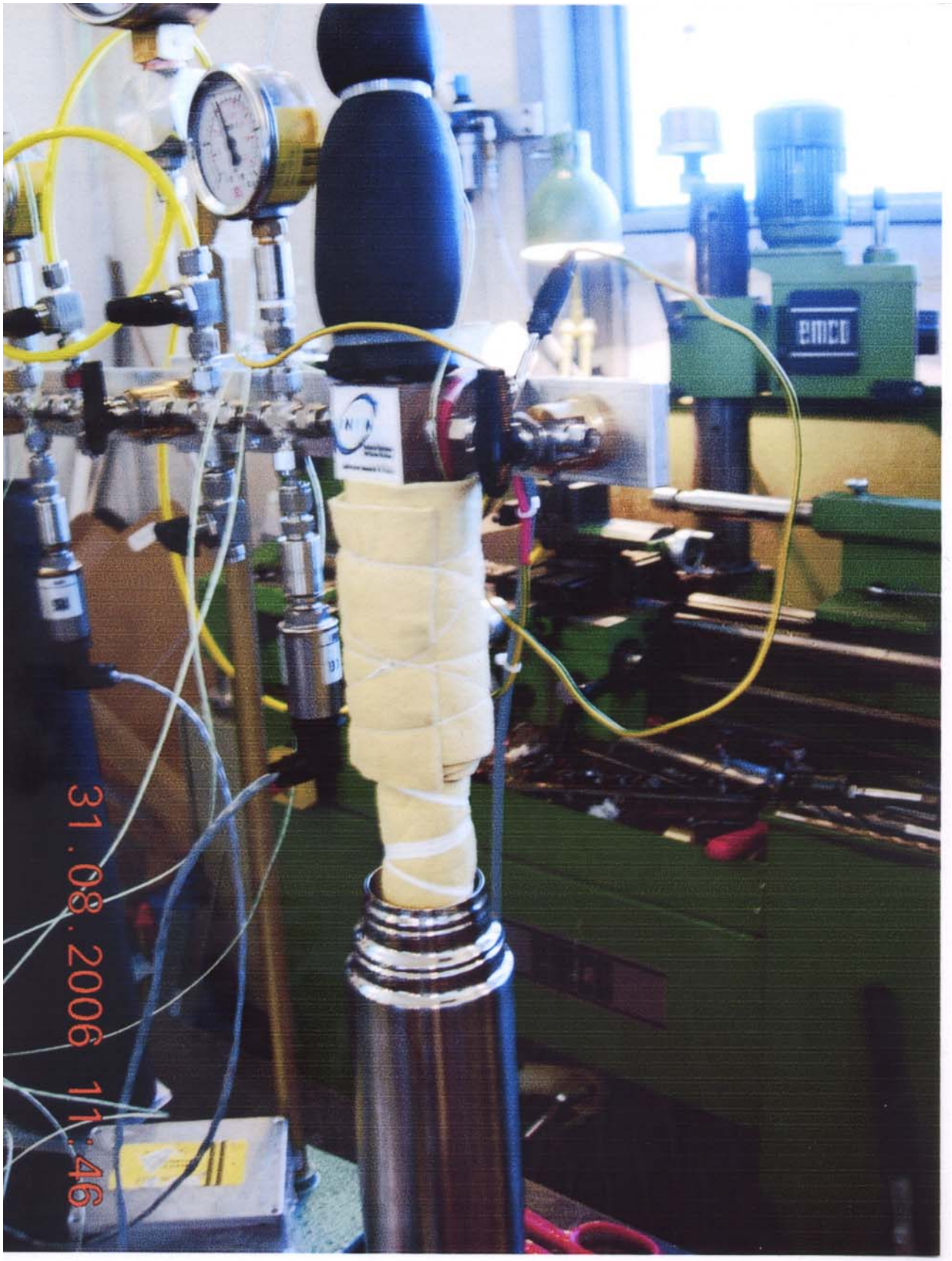

Fig. 17 Detail of Stainless Steel Dewar used as reaction chamber (-196°C≤T≤+350°C).

Fig. 18 Detail of hot finger put inside the crucible of chamber V2. The thermocouple is located in the middle of the copper section of hot finger.

Fig. 19 Detail of the multilayer reaction chamber V2 during assembling.

Prof. ARATA Experimental activity

In order to better understand Prof. Arata experimental activities, we give you as attachment to this file his article "*Development of "DS-Reactor" as a practical reactor of "Cold Fusion" based on the "DS-cell" with "DS-Cathode" – Presented at ICCF12 Conference (Yokohama, Nov 28÷Dec 4, 2005) printing by World Scientific (2006).*

In order to give the idea of the importance of nano-particles structures, we suggest to download the article of Arata from "Il Nuovo Saggiatore" at
http://www2.sif.it/riviste/nsag/nsag-2004-05-06/07.pdf
(pages 66-71)