EXCESS HEAT DURING DIFFUSION OF DEUTERIUM THROUGH PALLADIUM

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Abstract:
We have developed a mass flow calorimeter enabling us to measure accurately excess heat production during deuterium diffusion through the walls of palladium tubes. The experiment consists usually of a palladium tube 10 cm long, 2mm outer diameter with 200 µm thick walls, and closed at one end. Deuterium gas is introduced in the tube at various pressures, and temperatures and diffuses out through the walls of the tube. The tube, heated by a resistor, is positioned inside a reactor cell which is a small vacuum chamber. The reactor cell is positioned inside a second vacuum chamber. The outer walls of the vacuum chamber are water cooled. Thermal energy is determined by measuring inlet and outlet temperatures and water mass flow. The energy yield of this calorimeter is 95-98 % depending on input power.

We study the influence of deuterium pressure, tube temperature, various metal powders placed inside the tube, and metal deposited on the external surface of the tube. Our best result so far is an excess heat of 3 Watts with an input power of 47 Watts using an oxidized palladium tube filled with palladium powder. We propose a model involving reactions between D+ and D to explain our experimental results.

1- Introduction

Since the announcement of the discovery of Cold Fusion by Stan Pons and Martin Fleischmann (1) in 1989, researchers have tried all kinds of ways to reproduce and improve the experiment. Most work has been done by electrochemical means with solid electrodes in order to reproduce the original results. There are at least two major limitations to electrolysis in view of obtaining high energy outputs with little input power. On one hand electrochemistry in aqueous solutions and atmospheric pressure limits the cell temperature to 100 °C, and on the other hand lot of input energy is spent to dissociate water. There are certainly solutions to avoid these limitations, for example electrolysis with molten salts, or water at high pressure. However these technologies are difficult to implement in an ordinary laboratory.

More and more people are trying alternative solutions. One of them is the use of deuterium gas instead of heavy water. There are several advantages to that choice; one of the most important one is the fact that operations are feasible at much higher temperatures, and it is very likely that nuclear reactions in solids increase with increasing temperatures.

Most researchers have chosen solid metal electrodes as Pons and Fleischmann (1). However several experiments have been realized with either thin films or metal powders. Certainly the most interesting work has been produced by Arata and Zhang (2) with their DS cathode where a hollow palladium cathode is filled with palladium nano powder. They show large excess heat production when using heavy water and no excess heat with ordinary water. They have also measured production of helium-4 during these runs (3). Recently the same

authors have developed an alternative technique to obtain similar results applying high pressures of deuterium gas on the outside of a palladium tube filled with palladium nano powder. With this new design there is no energy spent to dissociate water and temperature can be larger than with an electrolytic design.

Another interesting result has been obtained by Li et al. (4). They observed excess heat when deuterium gas flows through a palladium foil. Interestingly, back in 1989, Fralick et al. (5) reported a similar experiment when they loaded an hydrogen gas purifier with deuterium, and then pumped it out. They observed a temperature rise with deuterium versus no temperature variation with hydrogen.

All these results indicate that diffusion of deuterium through palladium produces excess heat.

A weak point of Arata (2), Li (4) and Fralick (5) experiments is the lack of accurate calorimetry. In all three cases temperatures are measured, that clearly indicate excess heat, but no absolute value of the heat produced is given. Therefore we decided to build a calorimeter capable of doing experiments similar to the above, whilst keeping its capacity of good calorimetry.

This paper gives preliminary results of diffusion of deuterium through palladium. They show interesting features that need confirmation.

2 - Experimental setup

The main idea behind our calorimeter design is the use of a mass flow calorimetric method so that no calibration is necessary. Its design has been improved over time and it can be described in two different designs described below.

2.1 - First design

Figure 1 shows a view of the first system. The vacuum chamber is a stainless steel cylinder 7 cm in diameter and 50 cm long. It is surrounded by a second stainless steel envelope where 30°C water circulates at a constant flow rate of 180 ml/min. In and out temperatures of water are measured with two calibrated thermistors. A palladium tube closed at one end usually 10 cm long and 2 mm in outer diameter is welded on a 6 mm diameter stainless steel rod which is attached to a 6 mm diameter stainless steel tube with a Swagelok® fitting (figure 2). A thermocouple is inserted inside the stainless steel tube up to the center of the palladium tube when it is empty, and to its edge when it is filled with palladium powder from Goodfellow 80-180 nm. Therefore for a given heating power the measured temperatures differ according to the position of the thermocouple. The first value is closer to reality than the second one. Also because of the heat losses by conduction and non uniform heating, the temperature of the palladium tube is not uniform along the tube.

The palladium tube is heated by radiation with a Thermocoax resistor wrapped around it using DC current. Four stainless steel concentric reflectors are positioned around the resistor in order to minimize heat losses by radiation. Input heat applied to the resistor is dissipated mainly by radiation and is collected by the water cooled envelope. However part of the heat is lost by conduction through the 6 mm stainless steel tube attached to the palladium tube and also through the metal flange which holds the electric feedthroughs and the various pumping tubes.

A major flaw of this design is the fact that when deuterium gas diffuses out of the palladium tube, pressure inside the vacuum chamber increases. This also occurs when we purposely close the valve of the vacuum chamber towards the pumping system and let the pressure rise inside the vacuum chamber. Under these circumstances heat is transferred from the heater not only by radiation, but also by conduction and convection. This has been solved in the second design of the equipment described in the next section.

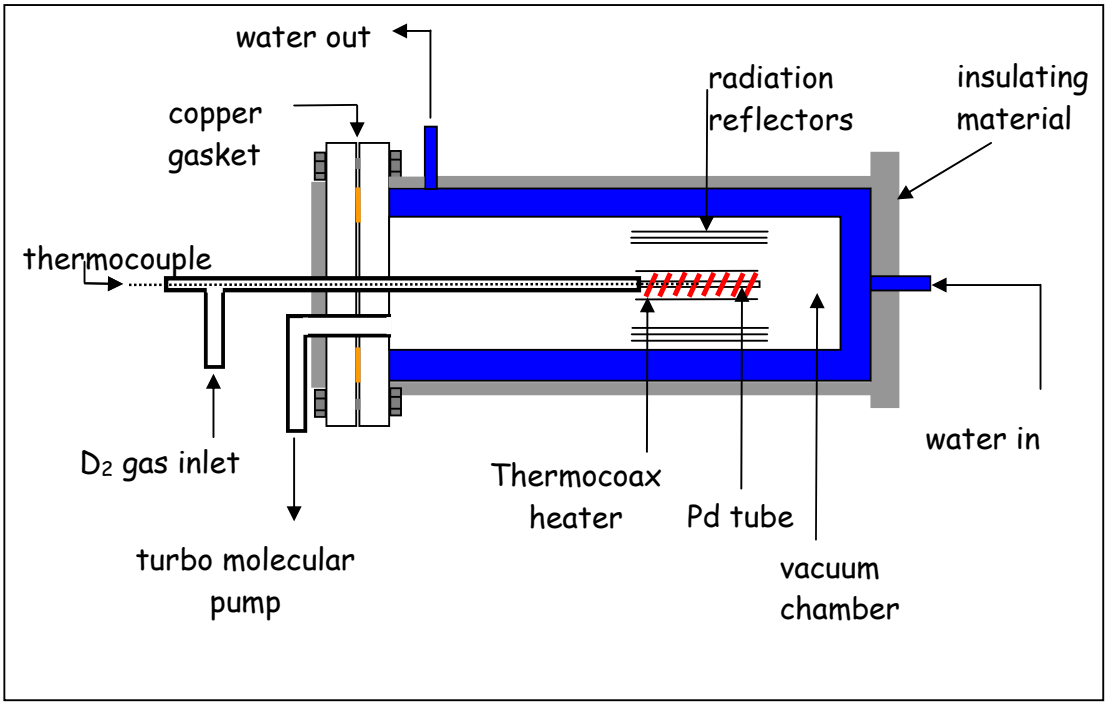

Figure 1
First design of the mass flow calorimeter

Figure 2
Top: photograph of the palladium tube attached to the stainless steel tube with a Swagelok® fitting. Bottom: photograph of the vacuum chamber

2.2 - Second design

In order to improve the calorimeter we have added a stainless steel reaction cell around the palladium tube, with a separate pumping system, so that there is no pressure rise in the vacuum chamber when deuterium diffuses through the palladium tube. Therefore heat is transferred from the reaction cell to the walls of the vacuum chamber by radiation only, independently of the amount of deuterium gas in the reaction cell. Figure 3 shows the new design. Figure 4 shows the palladium tube surrounded by the heater and a first radiation screen, as well as the reaction cell attached to the flange of the vacuum chamber

Also to improve stability versus room temperature we have added a water jacket around the whole chamber where water flows at the same temperature as in the cooling system.

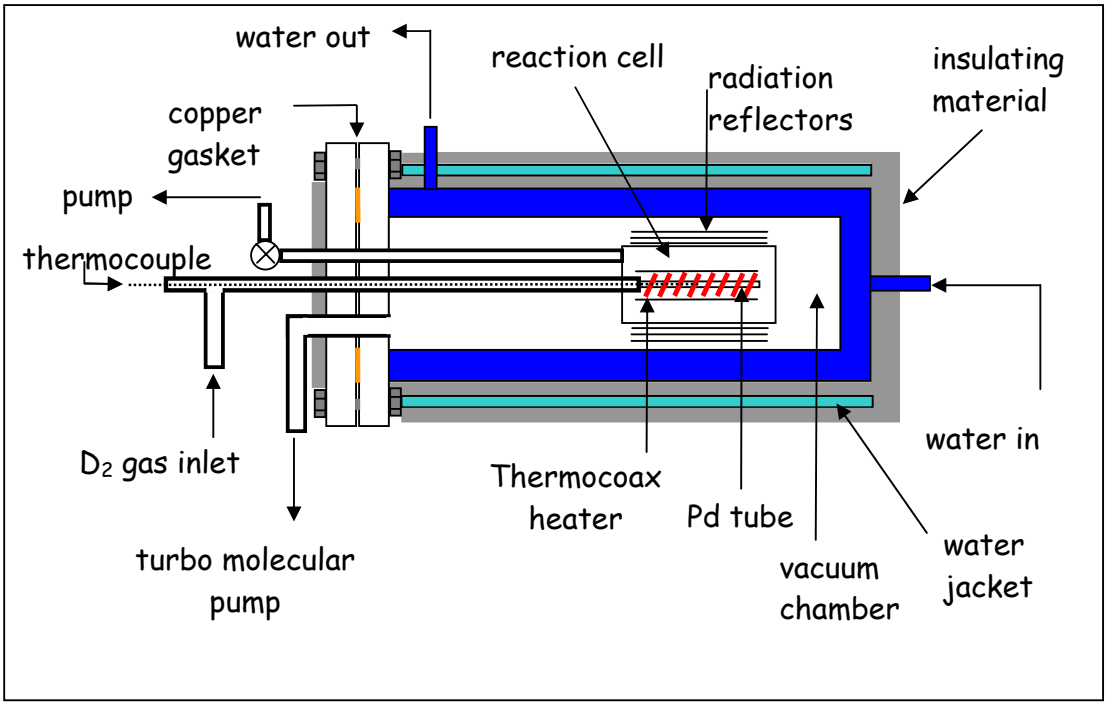

Figure 3
Schematic of the second design where a reaction chamber as been added as well as a constant temperature water jacket

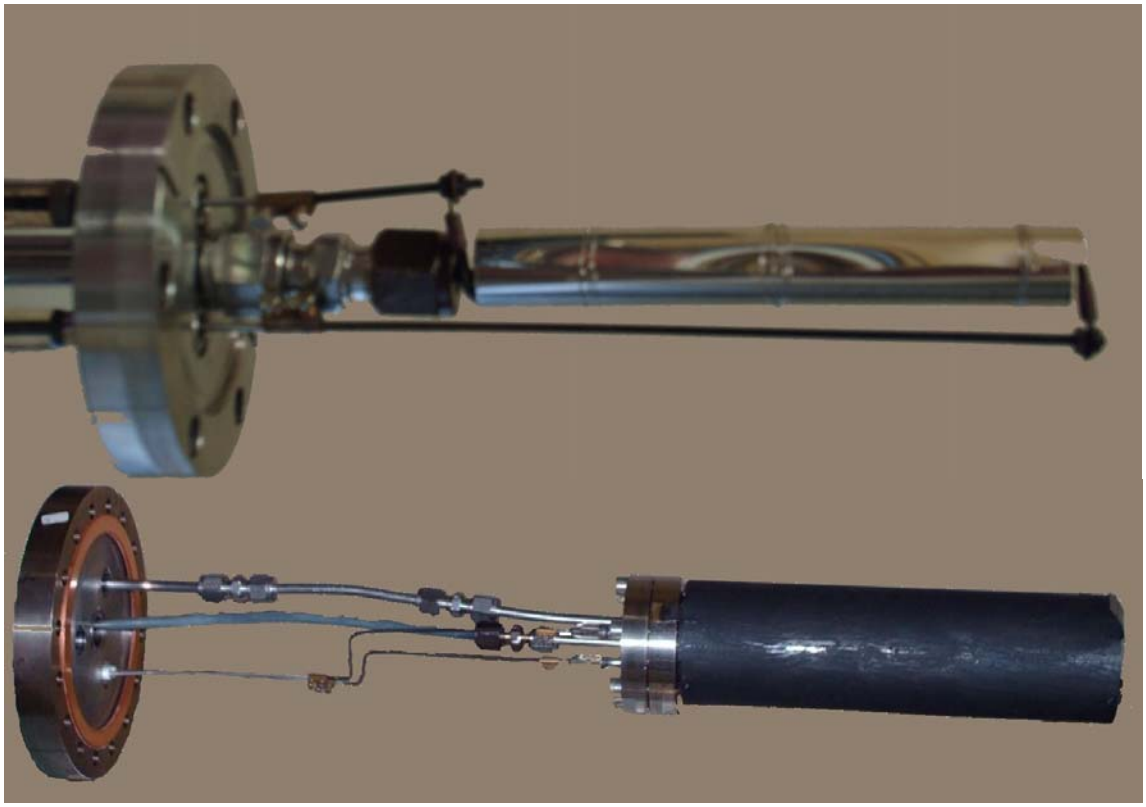

Figure 4
Top view: palladium tube surrounded by the heater and a first radiation screen.
Bottom view: the reaction cell attached to the flange of the vacuum chamber

2.3 – Calibration

Input power is measured accurately since the heater is driven by a DC power supply. Output power is measured via the temperature difference given by two thermistors, one at the inlet, and the other one at the outlet with a precision of +/- 0.01 K. De-ionized water mass flow rate is measured with accuracy better than 1%. As mentioned above, most heat is recovered by the water flow, and therefore taken into account in determining Pout. However some heat is lost through the large flange of the vacuum chamber which is not cooled by the water flow. In order to have an accurate value of the losses we have performed a blank run without the palladium tube. We replaced it with an open stainless tube. Our calibration shows that a correction of 5 to 2 % of the input power must be added to the output power to take into account the heat loss. This value varies with input power: the larger the input power the less correction is needed in percentage.

However in order to avoid having to perform this correction, it is even better to compare the output powers without deuterium and with deuterium. Therefore no correction is needed; we simply compare the two situations.

3 – Experimental results

So far, we have realized 23 experiments. The first 11 ones were with the first design and the following 12 with the second design. We have used mostly closed palladium tubes from Goodfellow, 10 cm long, 2 mm outer diameter and 200 μm thick walls. As we had a

limited number of such tubes, we had to use open ended tubes from Goodfellow that were brazed at one end. We also tried a Pd-Ag tube from Goodfellow, and in a couple of cases a stainless steel tubes filled with palladium powder, with a palladium carbon catalyst given by Case (6), and by beads similar to those of CETI (7). Our initial goal was to fill the palladium tube with palladium nano powder as Arata (2). However it turned out that the method they used Yamaura et al. (8), i.e. arc melting of a palladium zirconium alloy, then spin melting in order to produce an amorphous alloy followed by oxidation at low temperature was not available in our laboratory. Therefore we could not follow our initial goal of reproducing Arata's (2) work in its integrity. Instead we focused in other directions. We tried various alternatives: deposition of various metals such as gold, titanium or zirconium on the external surface of the tube, and letting deuterium gas diffuse out at various temperatures. We filled the palladium tube with palladium powder from Goodfellow without success. We tried to reproduce Case experiment using a palladium catalyst on carbon without success either.

For our last experiment with the first experimental design, run 11 we oxidized the palladium tube in air at 500°C for two hours, and filled it with palladium powder from Goodfellow. We did not observe any excess heat using our usual methodology: that is introduction of deuterium in the palladium tube at pressures up to 9 atmospheres, and simultaneously pumping out the vacuum chamber. For almost three weeks we tried operating at temperatures from room temperature up to 350 °C without success. At this point under three occasions as indicated on figure 5 we stopped pumping out the vacuum chamber and let deuterium pressure rise. This is when excess heat appeared as shown on figure 5.

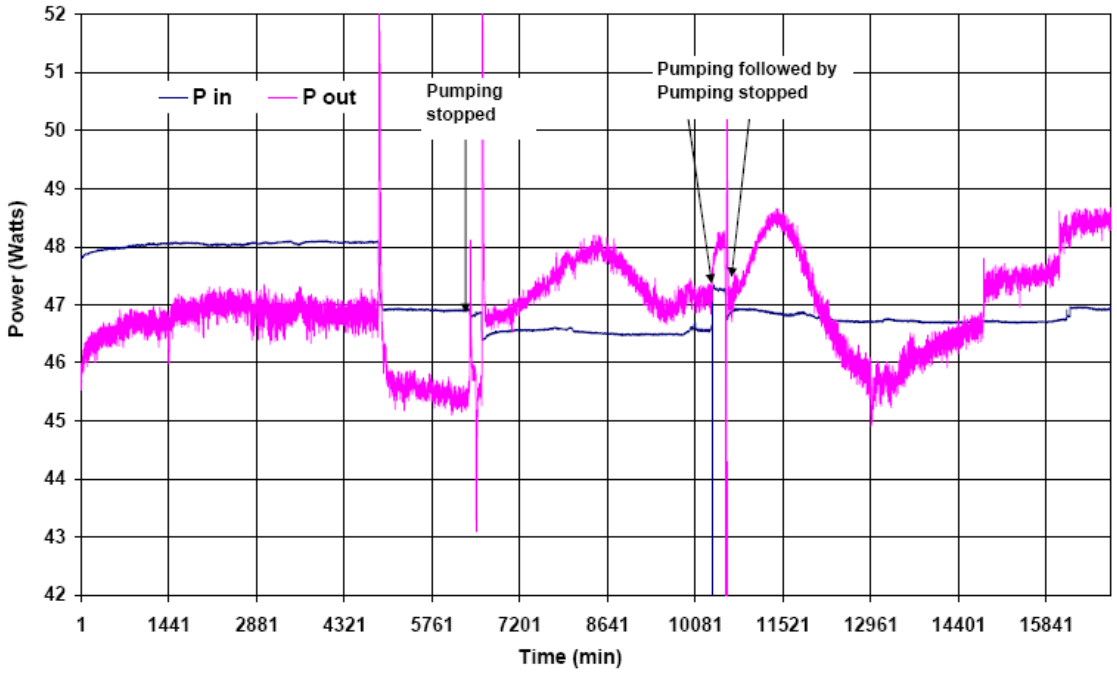

Figure 5
Powers in and out during the final phase of the experiment showing an uncorrected excess heat of 1.7 Watts

Before stopping pumping, Pout was about 1.2 Watt less than Pin. Therefore the actual excess heat observed should be increased by 1.2 Watt in order to obtain the correct excess

heat. When pumping was stopped we observed every time an increase of Pout followed by a decrease but Pout remained above Pin.

The immediate Pout increase appearing when the vacuum chamber valve is closed is due to the fact that heat accumulated on the palladium tube and on the heating device is evacuated by radiation only when the vacuum chamber is under vacuum. However when deuterium fills the vacuum chamber there is also conduction and convection that evacuate heat. Interestingly the last part of the experiment shows an increase of Pout after rise and fall that lasted three days. When the experiment was stopped the excess heat was 1.8 Watt without correction and 3.0 Watts when corrected for the losses in the calorimeter as explained above.

Temperature at the base of the palladium tube was 85°C before excess heat developed and gradually rose to 87 °C when excess heat appeared. This is a good indication that the effect is genuine.

Figure 6 shows SEM photographs of the original tube (left) and after oxidation (right).

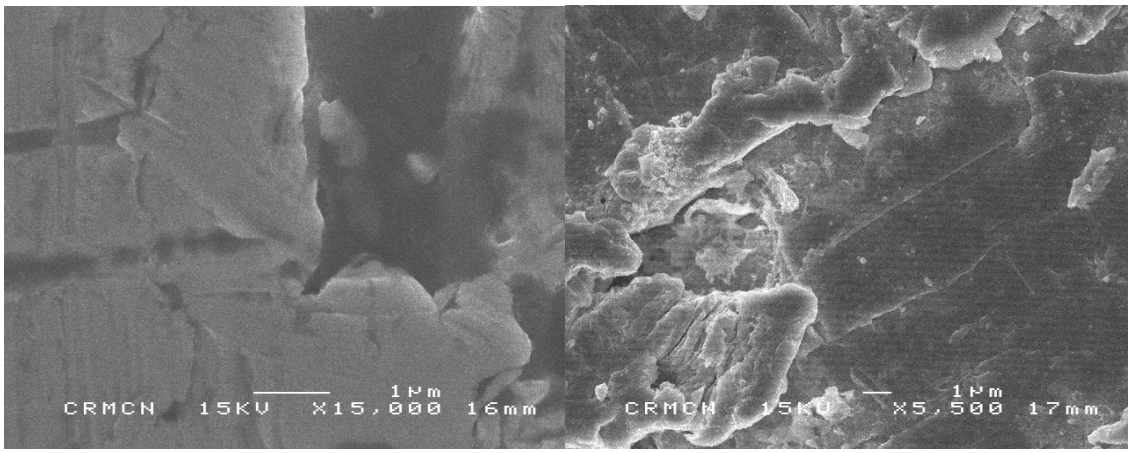

Figure 6
SEM images of the virgin palladium tube (left),
after oxidation in air for two hours at 500°C (right).

After the successful run 11, SEM images of the tube show interesting features (figure 7). It seems that some areas of the metal have melted and recristalysed. Palladium melts at 1553°C, and the highest temperature reached by the tube was 350 °C! X-ray fluorescence shows the presence of palladium only. No trace of other metal is visible. This is not surprising since X-ray fluorescence analyses a depth of one micrometer, whereas the amount of transmuted materials if any would be probably much less.

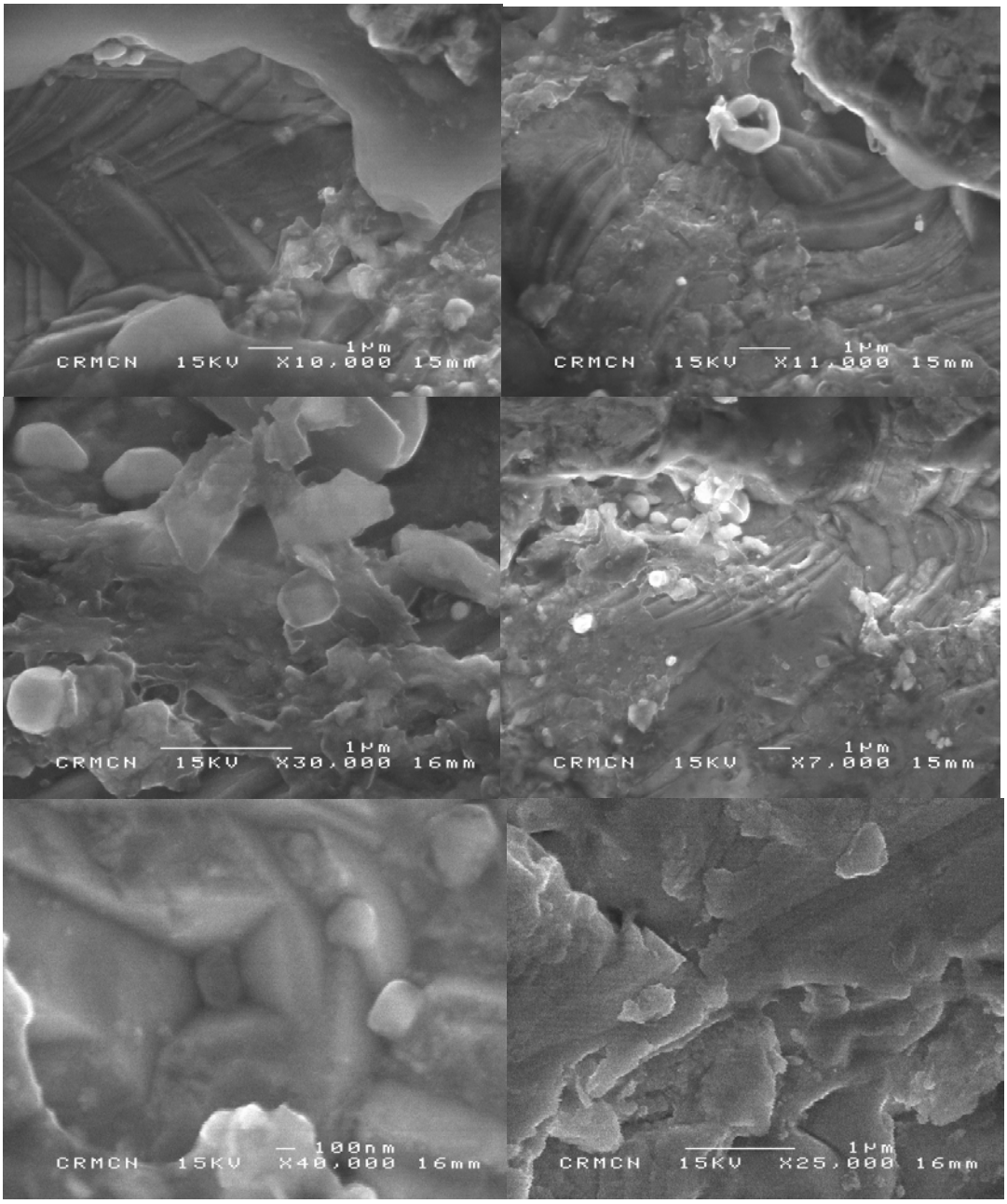

Figure 7
SEM images of the palladium tube run 11 that produced excess heat

In order to compare SEM images of run 11 that produced excess heat, it is interesting to compare them to those of a similar experiment that did not produce excess heat. Figure 8 shows SEM images of a palladium tube from run 20. The main difference between run 11 and 20 is the fact that the tube of run 11 was heated in air for two hours whereas the tube of run 20 was not. We do not observe the melted zone visible on figure 7.

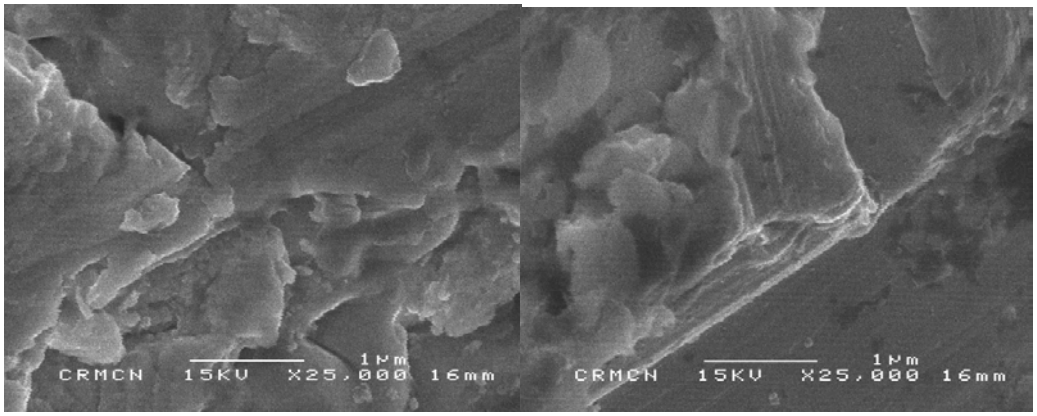

Figure 8
SEM images of the palladium tube of run 20 that did not produce excess heat.

4 - Discussion

We have shown that diffusion of deuterium through palladium produces excess heat. The best result was obtained when the tube was oxidized in air prior to starting the experiment, and filled with palladium powder. We measured an excess heat of 3 Watts with an input power of 47 Watts, i.e. a yield of 6% that lasted three days. However, it seems that the powder did not play a role in this experiment. In the future, experiments similar to run 11 will be performed without the palladium powder in the tube to verify this assumption.

It seems that in order to get excess heat we need the following conditions:

a) A flux of deuterium through the walls of the palladium tube.
b) The palladium tube should be oxidized by heating in air at 500°C.
c) The outer surface of the tube should be in a deuterium gas environment.

Our understanding of the mechanism that can explain our experimental results is as follows: deuterium molecules dissociate at the inner surface of the tube. Inside the palladium deuterium atoms ionize and D+ ions move towards the outer surface of the tube due to the pressure difference between the inside and the outside of the tube. When a D+ reaches the outer surface two options are possible:

a) In the first scenario, a D+ recombine with an electron to produced an adsorbed D atom at the surface of the metal, then this D atom meets another D and as soon as a D_2 molecule forms, it leaves the surface.

b) In the second case, lot more rare, a D+ ion would encounter an adsorbed D and would react with it to produce a Helium-4 atom. This is why the reaction is dependant on D+ flux through the palladium, and D coverage of the outer surface. The greater the flux, the more chances a D+ would interact with an adsorbed D. The reason why the palladium should be oxidized is probably due to the fact that either oxidation modifies the surface metallurgy, or oxygen atoms bring extra electrons that play a screening role.

An interesting question is how D+ can react with D. Our understanding is that electrons are not confined to a Bohr type orbit. Instead there is a non null probability that an electron orbiting a deuteron gets sometimes very close to the nucleus. Therefore for a short period of time the D atom is analogous to a shrinked atom. The incoming D+ can therefore get very close to the nucleus of the adsorbed atom. By tunneling a non null probability of reaction exists between the two deuterium nuclei. This reaction is happening at low speed, and it is

very likely that the two nuclei will configure themselves to react and produce maximum energy i.e. form a He-4 nucleus. Occasionally the other reactions producing neutrons and tritium might also happen. It is also possible that neutrons interact with the host metal and produces transmutations.

More work is necessary to confirm both our experimental results and also our model. We need to produce more excess heat in order to verify the formation of He-4. Our experimental set up is ready for such a work.

5 – Conclusion

We have developed a mass flow calorimeter that allows us to perform experiments in gas phase with deuterium or hydrogen. We have shown that with a palladium tube oxidized in air at 500°C, filled with palladium powder we could observe an excess heat of 3 Watts when deuterium gas flows through the walls of the palladium tube. We have developed a simple model that explains our experimental results.

Acknowlegments

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References:

(1) M. Fleischmann., S. Pons, Electroanal. Chem. 261, **1989**, p 301.

(2) Y. Arata, and Y. C.Zhang, Proc. ICCF12, Yokohama, edited by A. Takahashi, Y. Iwamura, and K. Ota, World Scientific **2006** p44-54

(3) Y. Arata, and Y. C. Zhang, Jpn. J. Appl. Phys. Part 2 38 (7A), L774, **1999**.

(4) X. Z. Li, B. Liu, N. Cai, Q. Wei, J. Tian, and D.X.Cao, in Tenth International Conference on Cold Fusion, editors Hagelstein, P. L. and Chubb, S. R. World Scientific Publishing Co., Cambridge, MA, **2003**, p. 113.

(5) G. C. Fralick, A. J. Decker, and J. W. Blue, NASA Technical Memorandum 102430, **1989**

(6) L. C. Case, The Seventh International Conference on Cold Fusion, Jaeger, F. ENECO, Inc., Salt Lake City, UT, Vancouver, Canada, **1998**, pp. 48.

(7) J.A. Patterson, US Patent #5,494,559, **1996**, System for electrolysis.

J.A. Patterson, US Patent # 5,318,675, **1994**, Method for electrolysis of water to form metal hydride.

G. Lonchampt, J. P.Biberian, L. Bonnetain, and J. Delepine, The Seventh International Conference on Cold Fusion, Jaeger, F. ENECO, Inc., Salt Lake City, UT, Vancouver, Canada, **1998**, pp. 202.

(8) S. Yamaura, K. Sasamori, H. Kimura, A. Inoue, Y.C. Zhang and Y. Arata, J. Mater. Res. 17, **2002**, 1929