TRITIUM PRODUCTION FROM PALLADIUM ALLOYS

T. N. Claytor, M. J. Schwab, D. J. Thoma, D. F. Teter and D. G. Tuggle
LAUR-98-2697
Los Alamos National Laboratory
MS C914
Los Alamos, NM USA 87545

ABSTRACT

A number of palladium alloys have been loaded with deuterium or hydrogen under low energy plasma bombardment in a system that allows the continuous measurement of tritium. Long run times (up to 200 h) result in an integration of the tritium and this, coupled with the high intrinsic sensitivity of the system (~ 0.1nCi/l), enables the significance of the tritium measurement to be many sigma (>10). We will show the difference in tritium generation rates between batches of palladium alloys (Rh, Co, Cu, Cr, Ni, Be, B, Li, Hf, Hg and Fe) of various concentrations to illustrate that tritium generation rate is dependent on alloy type as well as within a specific alloy, dependent on concentration.

1. INTRODUCTION

We report on a continuation of our tritium generation results from palladium wire-plate, and foil-wire configurations subjected to pulsed deuterium or hydrogen plasmas[1]. As in other work in this area[2,3], it has been found that the tritium output is very batch dependent and sensitive to material or gas impurities that prevent hydriding. These factors are not universally acknowledged and this has seemingly led many to believe that the experiments are not reproducbile, however it is very likely that many hidden variables exist in the materials and it may be that only certain small areas of the material are active.

Based on our previous work[1,4], it was apparent that the plasma-gas loading method to produce tritium in dueterided palladium was sufficiently well developed to initiate an alloy study. Some variability in the method still exists mainly due to several factors, primarily the inability to measure the insitu hydriding or temperature of the foil or wire and secondarily, the mechanical stability of the system (the wire as it hydrides sometimes bends away from the plate).

As before, due to the subtle and weak nature of the signals observed, we have taken many precautions and checks to prevent contamination and to confirm the tritium is not due to an artifact[5].

2. MATERIALS

For this work we used Cryogenic Rare Gases deuterium 99.995% that has 90 pCi/l of tritium, and research grade hydrogen with no detectable tritium (< 25 pCi/l). The major impurity in the deuterium is H2 (0.005%) (He <1ppm). A total of 7.3g of palladium wire/foil was used in plasma experiments described in this paper. Of that amount, 0.73g was used in various hydrogen or deuterium control experiments.

Most of the alloys described in this paper were made by a melt spinning (produces a tape) process. A boron nitride crucible was used to contain the molten palladium alloys and it cannot be excluded that nearly all the melt spun alloys contain some boron as an unintentional impurity. Several of the alloys were made in a batch process by arc melting powder on a

cooled copper block then homogenizing the alloys and subsequently rolling them into thin (220 microns) foils without intermediate annealing. Alloy concentrations are all given in weight percent.

Since these alloys were prepared from the same batch of palladium powder (Englehard) it is unlikely that tritium variation in any significant quantity would be found from melt spun batch to batch. One would expect either a uniform concentration or none at all. If, however, after the alloys were made, the alloys had been exposed to airborne tritium, one would expect the samples to show a prompt tritium signal upon hydriding with deuterium. The method used to test for contamination was to electrically heat the palladium to red-hot (>800 C) in deuterium or hydrogen and monitor the gas for tritium. In this way, no evidence of tritium (to within experimental error ~ 0.3 nCi) contamination was found. It should be noted that this method of removing hydrogen from tapes, foils and wire is very effective (as measured by sample resistivity).

3. APPARATUS

The two stainless steel gas analysis loops containing a 1.8 liter ion gauge and a 310.9 cc calibration volume have been described previously[1,4]. The atmospheric, ion gauge and sample pressure (0.2%), Femtotech and room temperatures (0.1°C) are recorded on a computer log at 60s intervals. Both loops have a heater to maintain the Femtotech (-0.045 nCi/l°C) at a constant temperature and there are valves that allow the pressurization of the cell independent of the loop. A two-micron filter is installed at the inlet of the ion gauge and at the outlet of the cell to eliminate spurious responses due to particulates. To eliminate the possibility of oil contamination, a molecular drag and diaphragm pump is used to evacuate the system.

A hydrogen oxidation system was built as a verification test for tritium using a scintillation counter (Packard 1600). Calibration D_2 gas with 25 nCi/l of tritium was used to test the two Femtotechs and the oxidation system. The two ionization systems agree to within 5% of each other while the scintillation results are within the experimental error (0.3nCi) of the Femtotechs.

The typical arrangement of the cell allows a tape or rectangular foil to sit perpendicular to and a few millimeters above a circular plate or a wire loop. In operation, the plasma is adjusted so that it envelopes about two thirds of the tape (or foil) and contacts the plate (or wire loop) at a small spot. Typically, the plasma is light blue (D_2^+) with areas of pink (D_3^+ or D_2^+) and extends up about 15mm from the tip of the tape or foil at currents of 2.5 to 4 A peak. Initially, the Pd sample is 25 to 30 mm in length and about one mm from the plate.

4. PROCEDURE

The procedure for a plasma run was to first fill the 3.1 liter loop with deuterium gas at 600 torr and obtain a measure of the initial background tritium concentration. Coincident with this, the cell would be pressureized with D_2 to pressures of 800 to 1000 torr to assist with a rapid hydrinding. With the loop drift rate measured, and the sample hydrided, the sample could be opened to the loop and the deuterium circulated through the cell and loop. The pressure in the cell and the loop was then lowered to the operating pressure by pumping the excess deuterium out.

The tape (or foil) was pulsed negatively, at 20 µs at 50 Hz, with currents between 2 and 5 A, voltages that varied from 1500 to 2500 V, and cell pressure of 280-350 torr. These conditions reduced the heating in the cell (foil temp ~75 to 125°C) and maintained a cell to ambient temperature difference of less than 25°C to avoid gross dehydriding of the wire and

plate. It appeared important to avoid a plasma condition that resulted in either a bright pink electron channel or arcing at the tip of the wire.

At the end of a run the pressure was increased to 600 torr, the gas was circulated, and the system allowed to equilibrate for about 8 hours. The system was then pumped out, the cell closed off, and fresh deuterium added to the system after one or two flushes with either fresh deuterium or air. The difference between the fresh deuterium and the deuterium reading after exposure to the plasma was used as the measure of the tritium content as well as the rate of tritium generation during plasma operation. Generally these two measurements agree unless another gas had been admitted to the loop.

5. RESULTS

A summary of the alloys and the tritium results are given in Table 1. The alloys were in the shape of small rectangular parallel sections usually 25-30 mm in length 2-3 mm wide and 25 to 220 microns thick. The opposing anode was a Goodfellow batch of wire 250 microns in diameter by 6 cm in length. Other metals can be used as the anode with little change in the results.

alloy composition	alloy type	Number of runs	highest tritium rate, nCi/h	significance
PdRhCoB (5%,3%)	melt spun batch 1	25	+0.080	43
PdRhCoB (5%,3%)	melt spun batch 2	2	+0.0062	7
PdRhCoB (5%,3%)	melt spun batch 3	1	+0.0051	4
PdRhCoB (5%,3%)	melt spun batch 4	2	+0.0017(0.0045)*	3
PdRh (10%)	melt spun	1	-0.00073	1
PdRh(5%)	melt spun	1	-0.0024	1
PdRh (0.5%)	rolled alloy	1	-0.00017	0
PdRh (0.1%)	homogenized, rolled alloy	1	+0.0048	2
PdCu (10%)	melt spun	2	+0.0062	3
PdCu (1%)	rolled alloy	2	+0.0014	1
PdHg (0.1%)	homogenized, rolled alloy	1	+0.0038	2.5
PdB (0.03%)	melt spun	2	+0.0001	0
PdB (0.06%)	melt spun	3	+0.0011	1
PdAl (0.1%)	rolled alloy	1	+0.0010.	1
PdFe (10%)	melt spun	1	+0.00062	1
PdNi (2.8%)	melt spun	1	+0.00053	1
PdCo (1.1%)	melt spun	1	+0.00025	0
PdW (0.1%)	rolled alloy	1	+0.00028	0
PdRhCr (5%,5%)	melt spun	1	+0.00021	0
PdLi (0.3%)	rolled alloy	1	-0.0028	2
PdBe (0.4%)	rolled alloy	2	-0.0028	2
PdBe (0.1%)	homogenized, rolled alloy	1	-0.0054	1
PdHf (0.1%)	homogenized rolled alloy	1	-0.0067	2
PdCr (1.1%)	melt spun	3	-0.00052	1
PdNi (1.1%)	melt spun	2	-0.0023	1

* new pulser and scintillation counting

Table 1. Palladium alloys and highest tritium rates observed during the plasma experiments

Most of the alloys did not produce tritium, only the PdRhCoB, PdCu, PdRh (0.1%) and PdB gave significant upward slopes. Surprisingly, several of the alloys, PdLi, PdBe, and PdHf produced distinctly negative slopes. It is unknown, at present, if this is due to actual tritium removal or a suppression of the background ion current. Note that the Rhodium series of alloys gives a negative slope at high concentrations and a positive slope at lower concentrations. This same effect was found before in technical grade palladium, in that

increasing the amount of impurities in the palladium is likely to suppress the tritium output. However, it appears that the copper and boron alloys at higher concentrations produced higher tritium output rates. More data should be collected in these two alloy systems to confirm these interesting results.
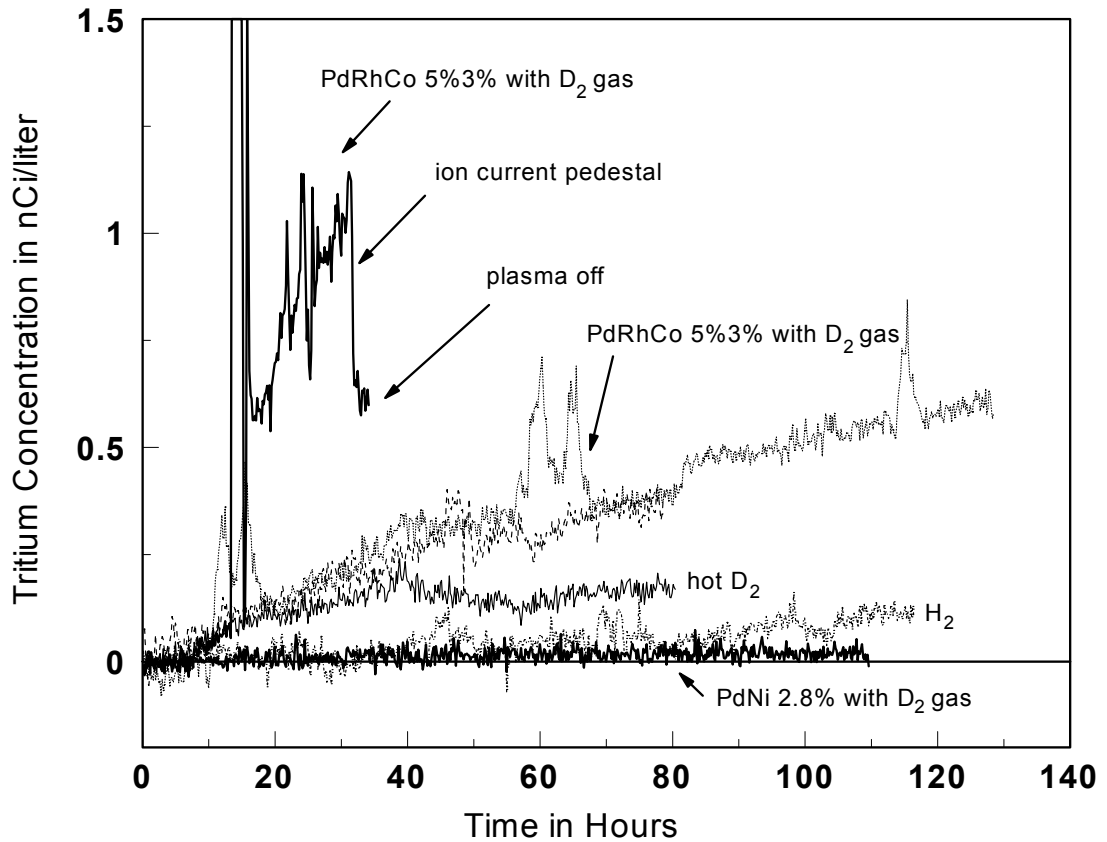

Figure 1. Tritium generation rates for various samples of PdRhCoB alloys and one PdNi sample using plasma loading/excitation.

Finally, we present the results from the PdRhCoB (5%3%~1%) alloy. This alloy was the most interesting alloy and the most prolific producer of tritium of any of the alloys investigated although not quite as good as some of the pure palladium batches investigated and reported on previously[4]. Shown in Figure 1 are the results of several different runs, three runs meant to be similar and one diverging downward from the others due to overheating by running the plasma duty cycle at 0.4% rather than the usual 0.1% starting at hour 39. There is also a run with hydrogen, that surprisingly is not identical to zero as is the PdNi 2.8% with deuterium. The spikes on the upper curve are due to pressure changes in the system that increase the sensitivity by increasing the pressure in the Femtotech. The very most upper curve has the highest rate of tritium output seen with any alloy and also shows a rare effect that has been noticed in one other plasma cell run with the same batch of material. This is the appearance of an additional ionization current. We attribute this to ionization in the cell because it rapidly disappears and then reappears if the flow is shunted away from the cell and then reestablished. A similar ion current can be produced if a collimated 25 mCi ^{241}Am source is placed next to the cell. However during the ion current excursion, no x-ray emission was noted over background outside the cell.

6. DISCUSSION

In our previous papers we have given a number of reasons for the fact that the detected ionizing material is tritium rather than an artifact of the instrument or some other isotope. Here we will not repeat the litany but merely refer back to those papers for details[1,4].

In addition to the arguments cited above we can add that the apparent tritium signal is material dependent and that certain palladium alloys exhibit a greater or less tritium production. Also, some of our older tritiated samples have been aged for about 18 months, long enough to measure the half-life and the spectrum. The results of these measurements are consistent with the half-life of tritium, 12.3y.

We previously[4] found that the tritium output was sensitive to metallurgical condition and impurity concentration of the palladium. Similarly, four batches of PdRhCoB made from the same initial batch of powder but were processed in a slightly different way such that batch 1 exhibited segregation, batch 2 and 3 were more completely homogenized and batch 4 was segregation free. Another complicating factor is that the boron concentration in the four PdRhCoB alloys is slightly different.

Since a short anneal will stress relieve the material but will not promote grain growth, it may be said that grain boundaries are important to the effect. Since impurities seem to play a role, it would appear that decorated grain boundaries are very important. The dislocation density in the material seems not to be critical since a high dislocation density is grown in to the material when it is hydrided.

It is very interesting to note that the Palladium Li alloys were inert in relation to producing tritium yet they hydrided very quickly and to reasonable level. In large part, the failure of most electrochemical loading experiments to produce tritium may be due to the ingress of lithium into the surface of the palladium from the LiOD used as the electrolyte. It should also be noted that tritium was produced (seemly reproducibly) by F. Will[6] using a D_2SO_4 electrolyte.

The fact that several impurities produce tritium weighs heavily against the hypothesis that these impurities take part directly in reactions since these reactions would all be energetic at the MeV level and thus generate high energy tritons that would interact with the deuterons to produce neutrons via the efficient dt reaction. If the reactions were simply dd, pt reactions assisted in some way by distortions of the lattice then one is still left with the problem of the excess energy of the triton from the dd reaction generating neutrons even if the dd n^3He branch is completely suppressed.

All of the samples and particularly the PdRhCoB samples were counted with a sensitive (~30 % eff) Ge-Li (aluminum encased) gamma detector but no lines over background were found in any samples.

7. CONCLUSIONS

The critical factor in the tritium yield is the purity and metallurgical condition of palladium. Alloys have been discovered that gave much enhanced tritium output over randomly selected materials. Unfortunately, not all the conditions necessary for a completely reproducible experiment are known at this time. The results presented here are encouraging in that it appears that designed materials may be fabricated that will reproducibly generate tritium and perhaps show other anomalous effects at measurable levels.

In summary, to achieve a measurable effect, the starting material must be free of tritium inhibitors, such as Li, or Be, the material has to have the proper level of enabling impurities at the grain boundaries, then the material has to be loaded to a modest stoichiometry and then subject to an excitation source such as electromigration or pulsed plasma discharge.

8. ACKNOWLEDGMENTS

9. REFERENCES

1. Tuggle, D. G., Claytor, T. N., and Taylor, S. F.; Tritium Evolution from Various Morphologies of Deuterided Palladium., Proceedings of the Fourth International Conference on Cold Fusion., December 6-9 1993, Maui, Hawaii., Ed. T. O. Passel, EPRI TR-104188-V1 Project 3170, July 1994, Vol. 1, p7-2.
2. Bockris, J. O'M., Chien, C-C., Hodko, D., Minevski, Z., Tritium and Helium Production in Palladium Electrodes and the Fugacity of Deuterium Therein, Frontiers Science Series No. 4, Proceedings of the Third International Conference on Cold Fusion., October 21-25 Nagoya Japan., Ed. H. Ikegami, Universal Academy Press Tokyo Japan., 1993, p231.
3. Romodanov, V., Savin, V., Skuratnik, Ya. Timofeev, Yu., Nuclear Fusion in Condensed Matter, Frontiers Science Series No. 4, Proceedings of the Third International Conference on Cold Fusion., October 21-25 Nagoya Japan., Ed. H. Ikegami, Universal Academy Press Tokyo Japan., 1993, p307.
4. Claytor, T. N., Tuggle, D. G., Taylor, S. F.; Evolution of Tritium from Deuterided Palladium Subject to High Electrical Currents, Frontiers Science Series No. 4, Proceedings of the Third International Conference on Cold Fusion., October 21-25 Nagoya Japan., Ed. H. Ikegami, Universal Academy Press Tokyo Japan., 1993, p217.
5. Cedzynska, K., Barrowes, S. C., Bergeson, H. E., Knight, L. C., and Will, F. W., Tritium Analysis in Palladium With an Open System Analytical Procedure, Fusion Technology, Vol. 20, No 1, 1991, p108, and private communication.
6. Will F. G., Cedzynska K., Linton D. C., Reproducible Tritium Generation in Electrochemical-Cells Employing Palladium Cathodes with High Deuterium loading, Journal of Electroanalytical Chemistry, Vol. 360, p161, 1993 .