

Deuterium Gas Charging Experiments with Pd Powders for Excess Heat Evolution

(I) Results of absorption experiments using Pd powders

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A twin system for hydrogen-isotope absorption experiments has been constructed to replicate the phenomenon of heat and ⁴He generation during D₂ gas absorption in nano-sized Pd powders reported by Arata and Zhang, and to investigate the underlying physics. For Pd-Zr oxide nano-powders, anomalously large energies of hydrogen isotope absorption, 2.4 ± 0.2 eV/D-atom and 1.8 ± 0.4 eV/H-atom, as well as large loading ratios of D/Pd = 1.1 ± 0.0 and H/Pd = 1.1 ± 0.3 , respectively, were observed during deuteride/hydride formation. The sample charged with D₂ also showed significantly positive output energy in the second phase after deuteride formation. Results for 0.1- $\mu\text{m}\phi$ Pd powder samples and Pd-black samples are also shown, for comparison.

Introduction

Arata and Zhang recently reported that highly pure D₂ gas charging of Pd nano-powders in the form of a Pd/ZrO₂ nano-composite induced significantly higher temperatures inside the reactor vessel than at the outside wall, continuing for more than 50 hours, while runs with H₂ gas showed almost no temperature difference.¹⁾ To verify that the excess heat originated in a nuclear process, a QMAS was employed to show the existence of ⁴He nuclear ash in the vessel and in the powder after the charging. The charging system is a sophisticated, yet simplified, version of Arata's previous-generation DS reactor²⁾. Successful replications using systems similar to the DS reactor with Pd-black have been reported^{3,4)}. This experiment has revolutionary implications, so it is extremely important to confirm the heat and ⁴He generation with fully quantitative confidence.

In the present work we constructed an experimental system to replicate the phenomenon and to investigate the underlying physics. An oxide mixture of Pd (34.6%)

and Zr (65.4%) was fabricated by Santoku Corp., Kobe, Japan. It has an average particle size of 7.7 μm , a specific surface area of 37.1 m²/g, and an average Pd grain size of 10.7 nm. If we assume perfect oxidation of the metal elements, a 10 g sample contains 3.0 g of Pd.

Experimental system

The D₂/H₂ absorption system is composed of two identical cells (which we designate an A₁·A₂ twin system). One cell is for the D₂ gas foreground run, and the other for the H₂ gas background run. As shown in Fig. 1 and Fig. 2 each cell has an inner reaction chamber containing Pd powder and an outer chamber that is evacuated to provide thermal insulation for calorimetry. A sheath heater and a copper cooling water pipe are wound around the outer surface of the reaction chamber. The heater is used to bake the sample powder, and the copper pipe is used for flow calorimetry. A pair of thermocouples is provided for the flow calorimetry to measure the difference between the inlet and the outlet cooling water temperatures.

The D_2 gas is nominally 99.5% pure and the H_2 is 99.998% pure. The D_2/H_2 gas is further purified by passing it through a liquid-nitrogen cold trap, and the flow rate is controlled by a Pd membrane, which also serves as an additional purifier. The Pd membrane (0.2 mm-t, 99.95%) separates the evacuated reaction chamber (50 mℓ) and the gas reservoir filled with D_2/H_2 at 1 MPa. The gas permeation rate is controllable between 0.1 and 25 sccm by varying the membrane temperature from room temperature to 900 K. All measured parameters are stored in a PC with a data acquisition period of 1 min.

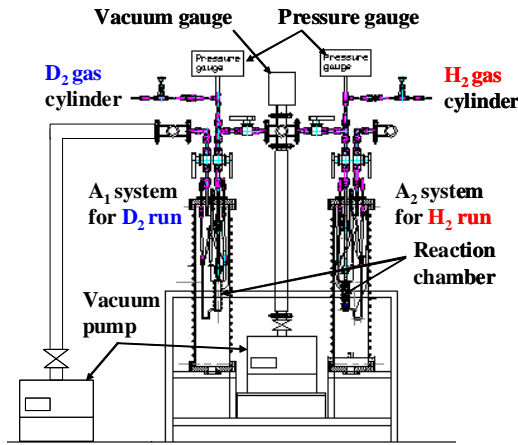


Fig. 1. Reduced view of the A₁-A₂ twin system

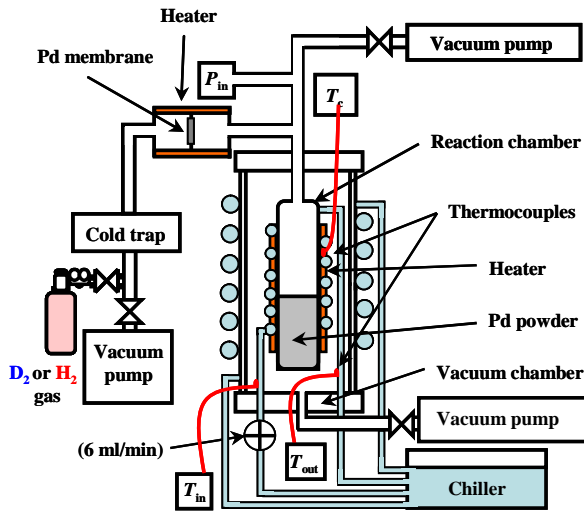


Fig. 2. Functional view of A₁

Preliminary experiments

To calibrate the flow calorimeter, we measured the heat recovery rate under a variety of conditions: with input power of 1, 3, 6 and 10 W, and D_2 gas pressure of 0, 0.1, 0.3 and 1.0 MPa in the reaction chamber. The coolant flow rate was 6 mℓ/min in all cases. The heat recovery rate was found to be almost independent of the pressure and the input power, with an average value of $63.1 \pm 5.8\%$. Temperature response to a stepwise variation of the input power was found to be expressed as a simple exponential function with a time constant of 5.2 min.

We examined temperature uncertainty and drift in a blank run with no sample powder in the A₁ chamber, but only H_2 gas at 1 MPa. The inlet-outlet temperature difference and the output power derived from it showed short-term fluctuations (Fig. 3). If we assume the experimental error in the present system is the standard deviation of the longitudinal data, the error or uncertainty for the output power and the integrated output energy measured for the A₁-A₂ system is 0.014 W and 0.83 kJ for a 1000-min acquisition period. A prototype system A₀ had a longer time constant and smaller sensitivity of heat measurement. It was used in the first stage experiments with the 0.1- $\mu\text{m}\phi$ Pd powder and Pd-black⁵⁾. In this A₀ system, temperature drift was sometimes observed, resulting in a larger error of 4.0 kJ for a 1000-min run.

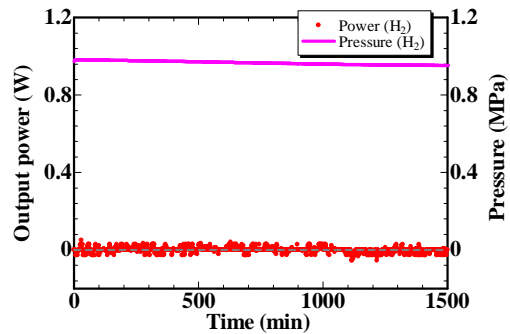


Fig. 3. Blank run with no sample powder.

Run number definition

In the following discussion, the run number is in the format “G-PN#M”, where: G is the gas species (D or H); P the powder species (PP, PB or PZ, explained below); N the powder identification number; and M the number of test cycles the powder was subjected to. Powder species include: PP (Pd powder with particle diameter of 0.1 μm and a purity of 99.5%); PB (Pd-black with a particle size of “300 mesh” and purity of 99.9%), and PZ (mixed oxides of Pd-Zr). For example, “D-PB2#3” represents: Deuterium (D_2) using palladium black (PB), sample number 2, which was subjected to 3 test cycles, the third of which is designated here.

Results with 0.1- $\mu\text{m}\phi$ Pd powder

In this section we describe absorption runs using the A_0 system for 5 g samples of 0.1- $\mu\text{m}\phi$ Pd powder. The reaction chamber filled with the powder was evacuated and heated for baking at 430 K. Then highly pure D_2 or H_2 gas was introduced into the reaction chamber through the Pd membrane filter. The procedures including evacuation, baking, and absorption constitute one cycle of test.

The results for the case of D_2 and H_2 absorption are compared in Fig. 4. After the gas was introduced, pressure did not begin to rise for a while. During this first phase the Pd powder absorbed almost all of the D_2 (H_2) gas atoms as they flowed in, and heat was released as a result of adsorption and formation of deuterides (or hydrides). After about 30 minutes, the powder almost stopped absorbing gas; the gas pressure began to rise, and the heat release from deuteride (hydride) formation subsided. This is the beginning of the second phase. The gas flow rate in the first phase is evaluated from the rate of the pressure increase at the beginning of the second phase. From the flow rate multiplied by the

duration of the first phase, loading was estimated to reach $\text{PdD}_{0.43}$ ($\text{PdH}_{0.44}$).

The output power is integrated over the first phase to give the output energies of 0.10 kJ/g-Pd(D) and 0.08 kJ/g-Pd(H), which are divided by the loading ratio of 0.43 and 0.44 to give the heat of formation ΔH_s of 0.24 eV/atom-D and 0.20 eV/atom-H, respectively. The values appear to be somewhat larger than those found in the literature⁶⁻¹⁰. However, they are consistent with each other, when we take into account that the differential heat of formation is an inverse function of the loading ratio; $\Delta H_s = 0.15, 0.12, 0.070$, and 0.061 eV/H for H/Pd ratio of 0.5, 0.55, 0.6 and $0.65^{9,10}$. The difference between D and H, the isotope effect, is rather large, but is not considered to be anomalous, since we find $\Delta H_s(\text{D})/\Delta H_s(\text{H}) = 1.25$ in ref. [9]. On the other hand, the output energies in the second phase (i.e.; the output power integrated over a second phase lasting 1,400 min) are smaller than the experimental error mentioned above, and the “excess heat” is not meaningful in this case. The results are summarized in Table I, which includes those for the Pd-black and the

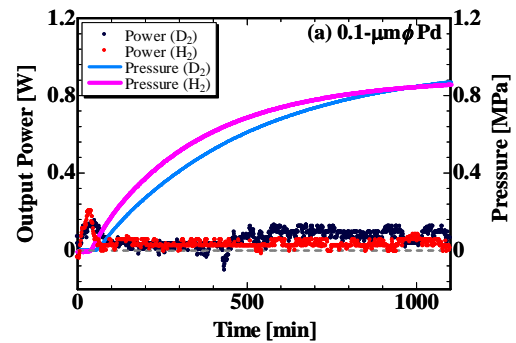


Fig. 4. Evolution of heat and pressure in the vessel after introduction of D_2 gas (blue/light blue) or H_2 gas (red/pink) to 0.1- $\mu\text{m}\phi$ Pd powder (D-PP1#1 and H-PP2#1). Power is slightly higher for D than H after 500 min.

Pd-Zr mixed oxide samples.

Results with Pd-black

The second kind of sample we tested is commercially available 300-mesh Pd-black whose surface has a kind of nano-scale fractal structure finer than the $0.1\text{-}\mu\text{m}\phi$ Pd powder. The performance of Pd-black absorption of D_2 using the A_0 system is compared with that of H_2 in Fig. 5. It is very interesting to note that: (1) much higher loading to $\text{PdD}_{0.88}$ or $\text{PdH}_{0.79}$ is realized, and (2) the output energies in the first phase, $E_{1\text{st}} = 0.67 \pm 0.12$ eV/atom-D and 0.62 ± 0.11 eV/atom-H, are 2 - 3 times larger than those for the $0.1\text{-}\mu\text{m}\phi$ Pd powder and those found in the literatures⁶⁻¹⁰. On the other hand, the output energy of 8.3 ± 4.5 kJ (2.6 ± 1.4 kJ/g-Pd) in the second phase of D_2 absorption appears to be larger than that in the case of H_2 . The difference is only marginal compared with the above-mentioned error due to the temperature drift of 5.5 K.

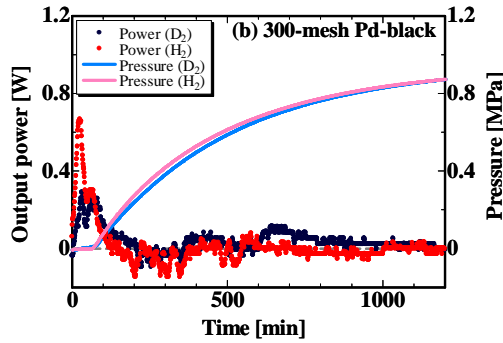


Fig. 5. Evolution of heat and pressure in the vessel after introduction of D_2 gas (blue/light blue) or H_2 gas (red/pink) to 300-mesh Pd-black (D-PB1#1 and H-PB2#1). Power is slightly higher for D than H in the second phase.

Using the improved $\text{A}_1\text{-A}_2$ twin system, we compared the performance of the Pd-black sample PB3 with a prolonged second phase duration of 4,500 min. We used the PB3 sample 3 times. The baking in the second cycle (#2) before absorption was at 440 K for 3 h, and the third (#3) at 570 K for 1 h. The results are shown in rows 6, 7 and 8 in Table I.

The first run (D-PB3#1) has essentially the same D/Pd ratio and energy output $E_{1\text{st}}$ as those with the A_0 system.

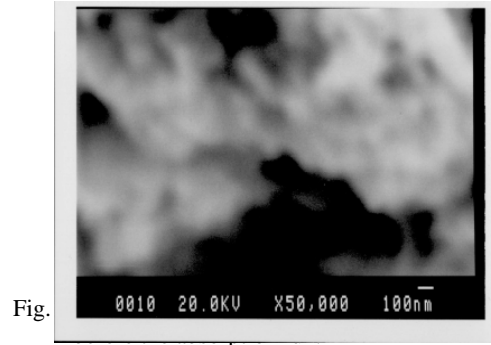


Fig. 6.

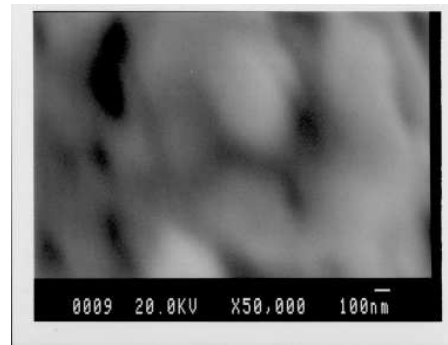


Fig. 7. SEM photograph of the surface of Pd-black after the absorption run.

Repeated use of the material retains nearly the same or even higher energy output $E_{1\text{st}}$ in spite of the significantly smaller D(H)/Pd ratio. This interesting fact could be related to some structural change in the sample. SEM photographs of the sample (Figs. 6 and 7) indicated clumping together and disappearance of the fine structure on the scale of several tens of nm.

The second phase results for Pd-black are close the system error of 4.0 kJ/1000-min for the A_0 system. This error is considered to be caused by a temperature drift, and might be applicable to the $\text{A}_1\text{-A}_2$ twin system too. The second phase results for Pd-Zr, described below, are stronger.

Results with Pd-Zr oxide compounds

The mixed oxides of Pd-Zr (PZ) that are thought to have even finer mesoscopic structure than the Pd-black

Table I. Comparison of absorption runs for the 0.1- $\mu\text{m}\phi$ Pd powder (PP), the 300-mesh Pd-black (PB), and the Pd-Zr nano-composite (PZ).

Row	Run number	weight of Pd [g]	Flow rate [sccm]	Output energy [kJ]		Specific output energy [kJ/g]		D/Pd or H/Pd (1 st ph.)	E_{1st} [eV/D(H)]
				1 st phase	2 nd phase	1 st phase	2 nd phase		
1	D-PP1#1	5.0	2.7	0.5 \pm 0.4	2.5 \pm 4.1	0.10 \pm 0.07	0.52 \pm 0.83	0.43	0.26 \pm 0.14
2	D-PP1#2	5.0	3.8	0.5 \pm 0.2	4.0 \pm 4.4	0.10 \pm 0.05	0.79 \pm 0.88	0.44	0.25 \pm 0.09
3	H-PP2#1	5.0	5.4	0.4 \pm 0.2	2.6 \pm 3.9	0.08 \pm 0.03	0.53 \pm 0.80	0.44	0.20 \pm 0.07
4	D-PB1#1	3.2	3.6	1.7 \pm 0.3	8.3 \pm 4.5	0.54 \pm 0.10	2.60 \pm 1.40	0.88	0.67 \pm 0.12
5	H-PB2#1	3.6	4.2	1.6 \pm 0.3	(-2.2 \pm 4.6)	0.45 \pm 0.08	(-0.62 \pm 1.30)	0.79	0.62 \pm 0.11
6	D-PB3#1	20.0	2.9	9.3 \pm 1.1	1.1 \pm 0.5	0.47 \pm 0.06	0.06 \pm 0.02	0.79	0.65 \pm 0.08
7	D-PB3#2	20.0	0.9	3.3 \pm 0.5	3.4 \pm 2.6	0.17 \pm 0.03	0.17 \pm 0.13	0.23	0.79 \pm 0.05
8	H-PB3#3	20.0	2.1	3.2 \pm 0.2	14 \pm 4.6	0.16 \pm 0.01	0.68 \pm 0.24	0.24	0.74 \pm 0.05
9	D-PZ#1	3.0	1.8	7.0 \pm 0.2	6.8 \pm 1.3	2.33 \pm 0.05	2.27 \pm 0.43	1.08	2.4 \pm 0.05
10	H-PZ2#1	3.0	2.3	3.6 \pm 0.1	(-5.1 \pm 1.4)	1.20 \pm 0.02	(-1.70 \pm 0.47)	1.00	1.3 \pm 0.02
11	D-PZ3#1	3.0	1.9	6.4 \pm 0.2	6.2 \pm 1.4	2.13 \pm 0.05	2.07 \pm 0.47	1.08	2.2 \pm 0.05
12	H-PZ4#1	3.0	3.6	4.8 \pm 0.1	1.9 \pm 1.4	1.60 \pm 0.02	0.63 \pm 0.47	0.86	2.1 \pm 0.03
13	D-PZ5#1	3.0	2.0	7.1 \pm 0.2	1.3 \pm 1.4	2.38 \pm 0.03	0.42 \pm 0.45	1.04	2.5 \pm 0.03
14	H-PZ6#1	3.0	5.9	7.1 \pm 0.1	(-0.2 \pm 1.4)	2.36 \pm 0.02	(-0.08 \pm 0.48)	1.34	1.9 \pm 0.02
Average			(D)	6.9 \pm 0.4	4.8 \pm 3.0	2.3 \pm 0.1	1.6 \pm 1.0	1.1 \pm 0.0	2.4 \pm 0.2
for PZ			(H)	5.2 \pm 1.8	(-1.1 \pm 3.6)	1.7 \pm 0.6	(-0.4 \pm 1.2)	1.1 \pm 0.3	1.8 \pm 0.4

samples (PB). The results of six runs using virgin PZ samples are summarized in rows 9 – 12 of Table I. Runs with the repeated use of the PZ sample will be discussed in the next paper¹²⁾ together with the above-mentioned PB samples. Using the A_1 - A_2 twin system, the runs H-PZ(2n)#1 were performed simultaneously with D-PZ(2n-1)#1, where $n = 1, 2$, and 3. The A_1 subsystem was used for D-PZ1#1, D-PZ3#1 and H-PZ6#1. In all runs, the PZ sample used was 10 g, and the baking temperature was 570 K for 3 h. The output energy in the second phase is the power integrated over 1,600 min. Examples of the evolution of the output power and the pressure for runs D-PZ1#1 and H-PZ2#1 are shown in Fig. 8.

We notice the following four facts in the first phase: (1) very large output energies that are more than 3 times greater than those for the Pd-black samples, (2) very large D/Pd (H/PD) ratios of 1.1 ± 0.0 (1.1 ± 0.3) that are even higher than those for the PB samples, (3)

surprisingly large $E_{1st} = 2.4 \pm 0.2$ eV (D) and 1.8 ± 0.4 eV (H) on the average, and (4) larger isotope effect in E_{1st} compared with those for 0.1- $\mu\text{m}\phi$ powder and Pd-black; the difference barely exceeds the error range determined from the standard deviation.

In two runs using H_2 , we obtained negative values for the specific output energy in the second phase, which was rather stable. This should be considered as due to a slight shift in the zero point of the thermocouple signal.

Finally, it should be mentioned that we observed nothing other than a steady background in the neutron counter and the scintillation probe located just outside the outer chambers.

More discussion and conclusions on these results and the underlying physics are given in our succeeding paper¹²⁾ in this Proceedings.

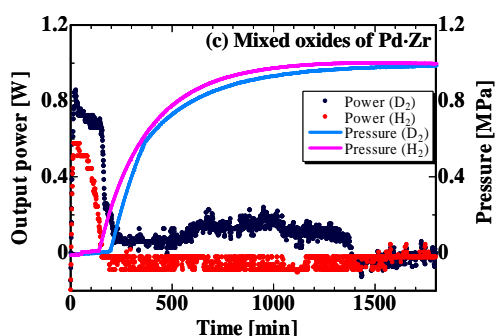


Fig. 8. Evolution of heat and pressure in the vessel after introduction of D₂ gas (blue/light blue) or H₂ gas (red/pink) to Pd-Zr oxide compounds (D-PZ1#1 and H-PZ2#1). Heat-power level by D is larger than that by H in the first phase and also in the second phase.

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