J. Condensed Matter Nucl. Sci. 8 (2012) 208–218

Research Article

Fabrication, Characterization, and Evaluation of Excess Heat in Zirconium–Nickel–Palladium Alloys

D.A. Kidwell *, M.A. Imam and D.D. Dominguez

Naval Research Laboratory, Washington, DC 20375, USA

Abstract

Prior gas loading experiments of Zirconium–Nickel–Palladium alloys have been reported to generate a greater amount of heat with deuterium than with hydrogen. What is intriguing about these experiments was the long-term heat observed. Others, using commercial materials of similar composition, have been unable to observe long-term heat. We also have been unable to observe long-term heat in the commercial materials and materials prepared at NRL. Furthermore, when tested using our gas-loading protocol of measuring both the heat during pressurization and evacuation, these alloys do not show much, if any, excess heat and the majority of the heat observed can be attributed to chemistry.

Keywords: Excess heat, Gas loading, LENR, Melt-spinning, Nanoparticles

1. Introduction

Zirconium–Palladium and Zirconium–Nickel–Palladium alloys were originally studied as hydrogen storage media [1–4]. In a number of publications, Arata and Zhang have reported that pressurizing these alloys with deuterium produces considerably more heat and for a longer period of time than does pressurization with hydrogen (Fig. 1) [1–3]. The excess heat was attributed to a Low-energy Nuclear Reaction (LENR) when the palladium nano-particles become loaded with deuterium. Kitamura and co-workers also performed similar experiments with commercially available catalysts and reported excess heat with deuterium compared to hydrogen but not long-term heat [1–3].

We have been using nano-particles of palladium and other metals in zeolites and on alumina supports that can be in the size range hypothesized to be necessary for good loading under moderate gas pressures. When these materials are pressurized with hydrogen almost all the heat is recovered upon depressurization (Fig. 2). In contrast, when the materials are pressurized with deuterium, only one-fourth of the heat is recovered. The ratio of $\mathrm{Heat}_{\mathrm{GasIn}}$:$\mathrm{Heat}_{\mathrm{GasOut}}$ can be up to eight for deuterium whereas hydrogen is invariably equal with any difference being attributed to oxygen impurities in the hydrogen [1].

*E-mail: David.Kidwell@nrl.navy.mil

Table 1. Heat of absorption (and spillover), Pd:H ratios, and estimated particle sizes for palladium prepared by various techniques. Data from Chen et al. [1] with particle size estimates calculated from dispersion measurements. The initial heat of adsorption appears higher than the approximate 100 kJ/mol value reported by Chou and co-workers with Pd on Alumina [1]. The different support may account for the higher heat measurements or Chou may have had larger particles.

Preparation	Estimated particle size (nm)	Initial heat of hydrogen adsorption (kJ/mol)	Ratio H:Pd at 0.2 bar
Pd powder	9	94	0.55
1.86% Pd/SiO_2	~ 4	92	0.68
10% Pd/SiO_2	1.1	131	0.9
5% Pd/SiO_2	1	183	1.05

The Zirconium–Palladium alloys of Arata and Zhang are claimed to have nano-sized palladium particles trapped in a zirconia matrix with the palladium particles estimated to be 5–10 nm in diameter [1]. Bulk palladium loads with hydrogen or deuterium to a Pd:D ratio of less than 0.7 at pressures of 500 bar [1]. The loading decreases with temperature and very slowly increases with pressure. Also, deuterium loads more slowly than hydrogen. In a previous paper, we discussed that results from electrochemical loading experiments of palladium indicate that the loading should be above a Pd:D ratio of 0.9 [1,2]. If this criterion is necessary to observe LENR for gas loading experiments in bulk palladium, the required pressure would be above 10^5 bar. As the palladium particles get smaller, the loading can increase rapidly (Table 1) but the size must be in the region of 1 nm or else the palladium acts like bulk material.

In gas pressurization experiments both the $Heat_{GasIn}$ and $Heat_{GasOut}$ must be measured. This eliminates reversible reactions and only irreversible reactions remain. Irreversible reactions may be chemistry (e.g., reduction of oxides or reaction of trace oxygen with hydrogen) or new physics (LENR). Frequently, relative rather than absolute temperature measurements are not made so that establishment of a stable baseline is important. Measuring both parts of the

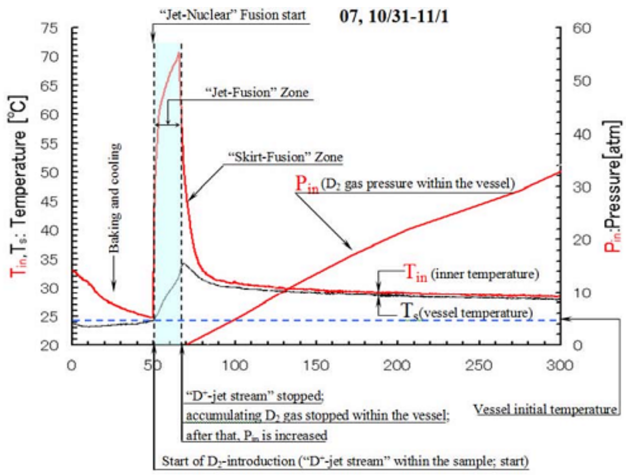


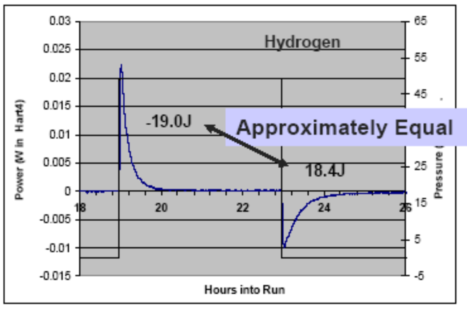
Figure 1. Results of Arata and Zhang on pressurization of Zr–Ni–Pd alloys. Note that much of the heat is generated during the first part of the pressurization. During the later long-term heat, the pressure is constantly increasing. The X-axis was not labeled in the original but is in minutes. Figure reproduced from Yoshiaki Arata and Y.-C. Zhang Establishment of the 'Solid Fusion' Reactor, *Proc. the 14th Int. Conf. on Condensed Matter Nucl. Sci. and the 14th Int. Conf. on Cold Fusion (ICCF-14)*, 10–15 August 2008, Washington DC, p. 756.

pressurization/depressurization cycle allows the temperature to return to baseline if long-term heat is suspected. Return of the temperature to the baseline upon removal of the gas is an important control as the system may have instrumental problems such as:

- Drift in the temperature of the room.
- Drift in the temperature measurement system.
- Inadequate initial baseline stabilization. The baseline should be taken while the system has air present (or better an inert gas such as helium) to reduce artifacts as:
  - The initial evacuation can remove materials, such as water, and be endothermic and change baseline.
  - Heat losses of the evacuated vs. pressurized cell must be considered due to conduction because hydrogen and deuterium have different thermal conductivities.

Several pressurization-depressurization cycles must be done to:

- Deplete chemistry (as chemistry could be confused as LENR)
- Indicate catalyst degradation by particle growth or poisoning, which is important for any practical use of technology
- Regenerate catalysts chemically (oxidation) or physically (heating) risks introducing new chemistry that may be interpreted as anomalous heat



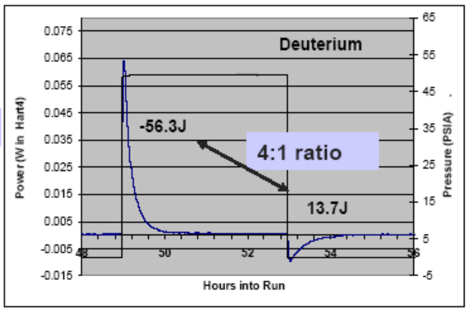


Figure 2. Typical pressurization cycles for nano-palladium in zeolite 13×. Pressurization with hydrogen the $Heat_{GasIn} \approx Heat_{GasOut}$ whereas with deuterium the $Heat_{GasIn} \neq Heat_{GasOut}$.

Gas pressurization experiments readily lend themselves to using hydrogen controls on the same materials. Hypothetically, LENR should not occur with all isotopes of hydrogen at the same rate. For good controls, they should be run under the same conditions as deuterium with the pressure, timing, temperature the same as possible and hydrogen being run first on fresh material to avoid D–H exchange reactions (D–H exchange on the Zr–Ni–Pd systems should be minimal as not much water or OH groups are present)[1]. Finally, gas pressurization techniques allow testing at several temperatures, which may be useful to distinguish chemistry from physics as generally reaction rates change with temperature.

After several pressurization-depressurization cycles, chemical reactions should be reduced in magnitude as the reactive chemicals are depleted. For the Zr–Ni–Pd systems, these chemical reactions include reduction of the palladium ions (as oxide) to palladium metal nano-particles and the formation of water from oxides (such as NiO). Ignoring small isotopic effects, both hydrogen and deuterium should produce similar chemical heats in the initial cycles. After this chemistry is depleted, the pressurization heat pulse can arise from three areas.

- Work of pressurization (PV work, the adiabatic temperature rise due to compression of the gas), which is reversible (recoverable) upon depressurization of the cell. However, to make accurate measurements, the rate of pressurization and depressurization should be similar. If the pressurization is slow, then the heat of pressurization can be at such a low value as to be misidentified as baseline drift. The magnitude of the heat of pressurization can be calculated [13].Other sources of heat due to chemistry such as the Joule–Thompson effect or ortho–para conversion are typically small. One form of chemistry that is not small and would be different with hydrogen vs. deuterium is D–H exchange, which was discussed in previous papers [13].
- Absorption of deuterium/hydrogen into the palladium particles and spillover onto the support. For nano-particles the absorption reactions can be quite rapid but the spillover can be slow. The possibility of spillover makes measurement of the Pd:D(H) ratio difficult, as not all the deuterium is associated only with the palladium [1–3]. Generally, particle size of palladium is best measured by probe molecules that interact poorly with the support [1]. The reverse reaction (desorption) from decomposition of the hydride and removal of spillover can be slow. In the case of palladium in zeolites, we have observed deuterium desorption hours after the start of the depressurization at 40°C, which makes accounting for all the reverse heat more difficult. However, the kinetics of desorption of hydrogen and deuterium are similar so that one can control for the other. Additionally, the number of moles of gas present after a few hours is small so that the total missing heat would also be small. Presumably, the deuterium/hydrogen is desorbed from the support first (spillover hydrogen) than only slowly from the particles. This makes resetting the particles difficult for subsequent pressurization/depressurization cycles, as discussed below in Fig. 6.
- New physics such as LENR.

Similar systems to the Zr–Ni–Pd alloys of Arata et al. such as Zr–Ni alloys, have also been studied as hydrogen storage materials [1]. The Zr–Ni alloys take-up considerable hydrogen in a very exothermic manner at higher temperatures when zirconium metal (as opposed to the oxide) is present. The long-term heat shown in Fig. 1 could have been produced by chemical processes. The continually and slowly increasing pressure allows new chemistry to occur (e.g. formation of hydrides in larger and larger particles). As the endothermic heat during depressurization is not measured, partially reversible reactions such as hydride formation may be overlooked. Additionally, if the palladium nano-particles needed to be in a size regime of 1 nm (much smaller than reported by Arata et al. for their palladium alloys) to load sufficiently, then these systems should not load to high levels of deuterium and consequently not work. Even with these experimental deficiencies, the results were intriguing. We made a series of Zr–Ni–Pd alloys by a similar process as described by Yamaura and characterized them by X-ray diffraction (XRD), Thermogravimetric Analysis (TGA), and gas pressurization experiments at various temperatures. By recording both the $Heat_{GasIn}$ and $Heat_{GasOut}$ and running hydrogen controls, we found that the large amount of heat generated with these types of materials is likely chemical in

Table 2. Alloys prepared. The italicized values for the alloys produced the most heat during pressurization.

Zr (%)	Ni (%)	Pd (%)
69.5	30	0.5
69	30	1
68	*30*	*2*
64	30	6
70	30	0

origin.

2. Experimental

The alloys Zr–Ni–Pd with different compositions were prepared by arc melting of high-purity elements (3 N) in an argon atmosphere using a water-cooled copper hearth. Alloy ribbons were then fabricated from these ingots by a single-wheel melt-spinning technique as shown in Fig. 3. A quartz crucible with an orifice of about 0.75 mm and a Cu wheel with a surface velocity of 45 m/s were used to produce ribbons with a width of $\sim$2 mm and thickness of $\sim$20–40 μm.

Various alloys were prepared as listed in Table 2. After preliminary tests, the Zr68–Ni30–Pd2 alloy produced the most heat so it was prepared in a large batch and used for all the tests presented here. The heat treatment conditions are listed in Table 3. The percent oxidation was determined from weight gain by assuming that all the weight difference was due to oxygen uptake and that only Pd and Zr was oxidized. Percentages above 100 indicate partial oxidation of the nickel. The amount of oxide formation varied even under similar conditions (compare samples 3 and 6).

Thermogravimetric analysis (TGA) was performed using a TA Instruments Q600 TGA/Differential Scanning Calorimeter (DSC). Measurements were determined by heating approximately 50 mg samples from room temperature to 1000°C at a rate of 10°C min^{-1} in air flowing at 50 cm^3 min^{-1}. Figure 4 shows a TGA–DSC analysis of one alloy. Note that the oxidation only occurs readily after about 500°C.

Pressurization cycles were either done in a precision oven system or a Hart calorimeter, both with an automated manifold and custom collection electronics and software, as described elsewhere [13].

XRD samples were taken on a Bruker D8 Advanced and are shown in Fig. 5 for a before and after sample. Not much change in the diffraction pattern is evident. However, note that even though ZrO_2 dominates the XRD spectra, this batch of material was only 37% oxidized.

An attempt to measure radiation was conducted on a sample of Zr68–Ni30–Pd2 alloy heated to 510°C for 17 h (21% oxidized, not shown in Table 3). Thermal measurements taken concurrently to the X-ray measurements showed heat evolution. An AmpTek XR-100CR thin beryllium window Si–PIN X-ray detector was mounted though a Cajon seal directly over the powder contained in plastic cap along with a NTC thermistor. The system was sealed with O-rings, evacuated and then pressurized. The deuterium pressure was limited to 2 bar to avoid damaging the Be window. No increase in radiation during pressurization was observed.

3. Results and Discussion

Initially, we prepared our alloys as outlined by Yamaura et al. [1], but found that these materials did not absorb hydrogen or deuterium. However, after a series of tests, air oxidation at approximately 500°C, rather than 280–400°C in the Yamaura ptrotocol, allowed some materials to absorb hydrogen in an exothermic reaction [2]. Extended periods of oxidation reduced the hydrogen reaction and short oxidation times made materials that were hard to crush. After