



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.

© 2012 ISCMNS. All rights reserved. ISSN 2227-3123

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 $\text{Heat}_{\text{GasIn}}:\text{Heat}_{\text{GasOut}}$ 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 10⁵ 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

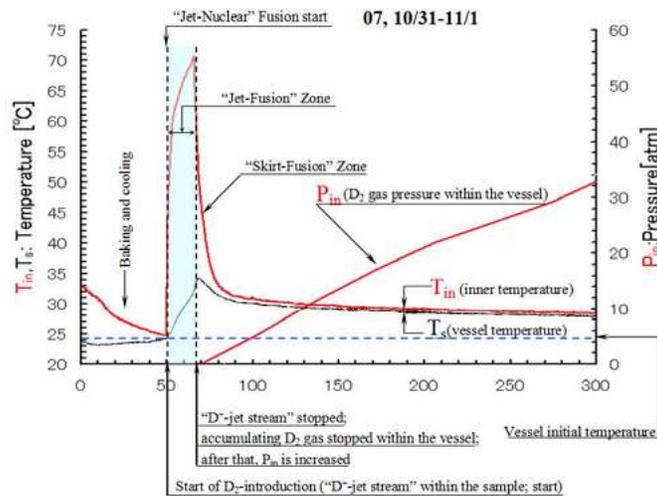


Figure 1. Results of Arata and Zhang on pressurization of Zr–Ni–Pd alloys. Note that much of the heat is generated during the first part of the pressurization. During the later long-term heat, the pressure is constantly increasing. The X-axis was not labeled in the original but is in minutes. Figure 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

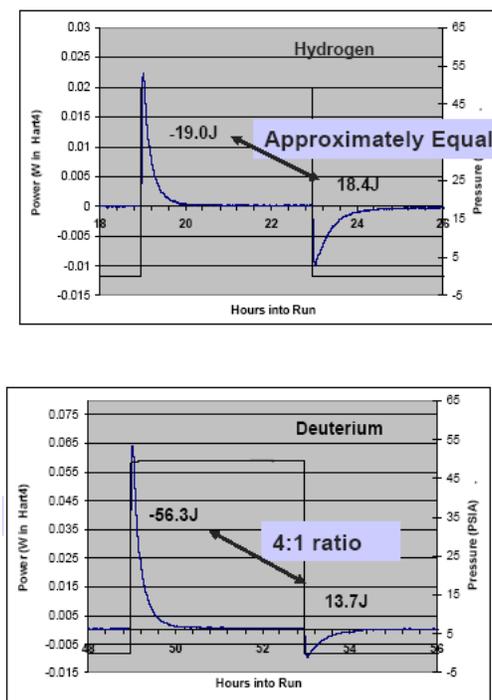


Figure 2. Typical pressurization cycles for nano-palladium in zeolite 13 \times . Pressurization with hydrogen the $\text{Heat}_{\text{GasIn}} \approx \text{Heat}_{\text{GasOut}}$ whereas with deuterium the $\text{Heat}_{\text{GasIn}} \neq \text{Heat}_{\text{GasOut}}$.

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 $\text{Heat}_{\text{GasIn}}$ and $\text{Heat}_{\text{GasOut}}$ 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
<i>68</i>	<i>30</i>	<i>2</i>
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 ~2 mm and thickness of ~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 cm³ 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 ZrO₂ 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 through 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 protocol, 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

Table 3. Heat treatment conditions and oxidation percentage for Zr68–Ni30–Pd2. The italicized values for the sample conditions produced materials that showed the most heat during pressurization.

Sample number	Temp/time	% Oxidation to ZrO ₂ and PdO
2	513°C/2 h	11
1	513°C/20 h	37
5	<i>675°C/2 h</i>	<i>19</i>
3	675°C/20 h	85
6	675°C/20 h	101
8	780°C/2 h	40
7	780°C/20 h	148

exposure to deuterium/hydrogen the alloys became finely divided when heat was produced and retained the original texture when only minor heat was produced.

A pressurization cycle for four selected samples from Table 3 is shown in Fig. 6. Only sample 5 showed substantial heat and was finely divided when removed. The integrated heat for pressurization/depressurization cycles at various temperatures is shown in Fig. 7. Note that in the first cycle, a very large heat pulse was observed during pressurization. Additionally, $\text{Heat}_{\text{GasIn}} \gg \text{Heat}_{\text{GasOut}}$. What appears to be happening is that a chemical reaction occurs during the first exposure to deuterium/hydrogen, likely due to reduction of oxides and absorption of deuterium/hydrogen into the matrix. At 40°C, the desorption of deuterium/hydrogen is very slow so that in subsequent cycles, that heat is missing. Monitoring the pressure and gases during evacuation also indicates that deuterium/hydrogen is constantly evolving. At higher temperatures, the removal of deuterium/hydrogen occurs more readily but is still somewhat slow. Even at 200°C, the heat evolution does not display a single exponential (Fig. 6, inset). Desorption of spillover deuterium/hydrogen followed by slow removal from hydrides in the matrix may account for the shape of this desorption curve.

Of the seven samples examined, only sample 5 exhibited substantial amounts of heat. The heat observed for sample No. 5 was 20–100× larger than observed for the Pd on alumina or Pd in zeolites [13]. To quantify the heat, an aliquot of Zr68–Ni30–Pd2 (heated to 650°C for 3 h 15 m, 66% oxidized) was run in the Hart calorimeter at 40 °C and found

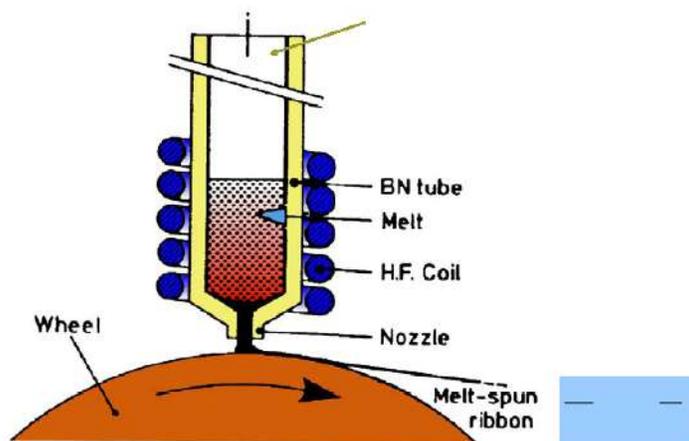


Figure 3. Melt-spinning set-up.

to be about 339 J/g. Water formation was minimal as measured by the RGA. Arata found larger amounts of heat (550–1000 J/g) with his Zr64–Ni30–Pd6 depending on his experimental protocol [22]. All these numbers are LESS than has been calculated for the reaction $\text{Zr}_2\text{Ni} + 2.25\text{H}_2 \rightarrow \text{ZrH}_2 + \text{ZrNiH}_2$; (-274.4 kJ/mol [21] or 1138 J/g), ignoring the approximately 10 J/g contribution from the formation of PdD with Pd at 6% [21]. *Therefore, chemistry can account for ALL the abnormal amounts of heat during pressurization and no new processes need be invoked.* Kitamura and co-workers also saw large amounts of heat during pressurization of Zr65.4–Pd34.6 (the depressurization, endothermic reaction was not measured) [8]. They observed slightly more heat with deuterium than hydrogen but the pressurization rates were not the same. They calculated an energy of 2.4 eV/Pd atom, which would be beyond chemistry, but they attributed all the heat to reaction only with palladium rather than the whole matrix [2].

Both Kitamura and our work used materials prepared as described by Arata et al. In catalysts preparations, it is possible that impurities or slight procedural changes will affect the catalytic activity. It is possible that Kitamura and our results would be different if the same catalyst was tested. However, there are several procedural issues with the experiment by Arata and Zhang depicted in Fig. 1. (1) The endothermic heat during depressurization was not measured. (2) The pressure was continually and slowly increasing, which performs PV work on the system producing heat (should be small). However, the higher deuterium pressures allow new chemistry to happen and because the endothermic heat during depressurization was not measured it is difficult to separate the chemistry of deuterium absorption and adsorption and PV work from LENR. The long-term heat was also not measured for a sufficiently long time to unambiguously determine that chemical energy is not being observed. Having the heat decrease in an exponential manner looks suspiciously like the depletion of a chemical reaction. (3) Few hydrogen controls were reported to help elucidate chemistry. (4) It was not clear from their papers or presentations if the samples were cycled so that the presented data may be due to reduction of oxides, which in the case of nickel and palladium is exothermic. Kitamura and coworkers did cycle a palladium black sample three times. The first cycle was higher but after this cycle, the deuterium and hydrogen numbers were the same [8]. They did not cycle their Zr65.4–Pd34.6 system.

In the Zr–Pd or Zr–Ni–Pd systems, if the sample was partially oxidized, there would be enough chemical energy present to account for the observed heat. Air oxidation using Yamaura's protocol [2] leaves considerable metallic zirconium present. Determining the oxidation state of the zirconium from only the XRD spectra is difficult as it can

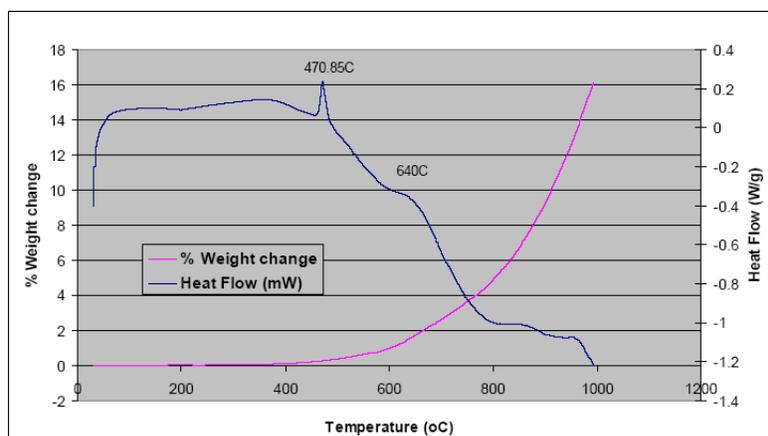


Figure 4. Thermal Gravimetric analysis of Zr68–Ni–30–Pd2. Most of the weight gain occurs above 600°C, showing that lower temperatures do not oxidize the Zr. Similar results were observed for the 6% Pd alloy, but the exotherms at 470°C and 640°C were much larger.

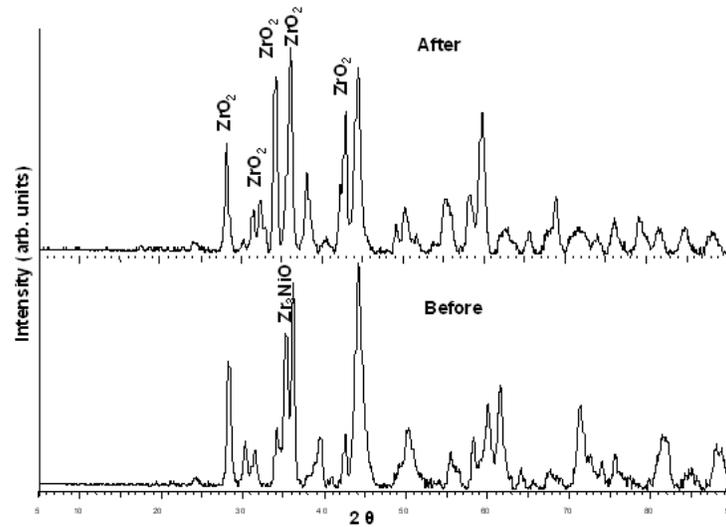


Figure 5. The XRD patterns of Sample 1 (Table 3) before and after cycling. The spectra are dominated by phases of ZrO₂ even though it was incompletely oxidized. After cycling certain oxides are reduced, which makes the ZrO₂ appear larger.

miss amorphous regions such as present in melt-spun alloys. The data in Fig. 6 illustrate why cycling and measurement of both Heat_{GasIn} and Heat_{GasOut} is important. Stopping with the initial pressurization may miss important chemistry and lead to the incorrect conclusion that the heat is due to a non-chemical process. Also, attributing all the heat to only a single chemical species, such as palladium, is clearly in error. Not measuring the heat absorbed during depressurization can miss reversible chemical reactions such as hydride formation. Likewise, having similar amounts of heat generated for deuterium vs. hydrogen (at 300°C in Fig. 7) implies a chemical process rather than new physics, such as LENR, as similar rates of some kind of unknown nuclear event are unlikely with both deuterium and hydrogen.

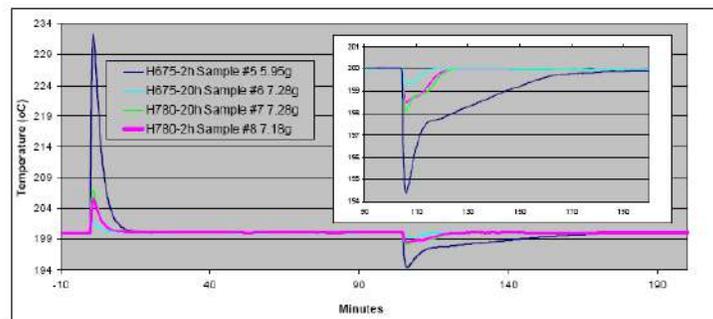


Figure 6. Typical deuterium pressurization/depressurization cycle for four samples (Nos. 5–8) from Table 3 carried out at 200°C in a precision oven. This cycle was taken after several other cycles at lower temperatures depleted the irreversible chemistry. Note the absence of long-term heat as the heat pulses return to the baseline.

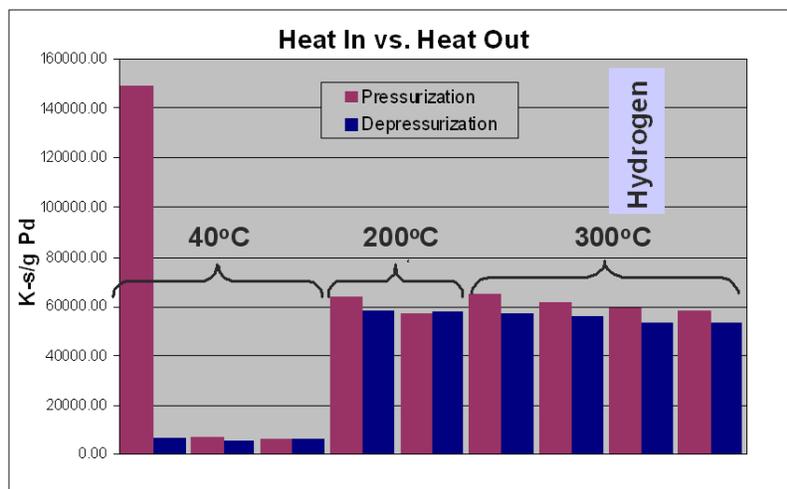


Figure 7. Integrated temperature curves for Sample No. 5 at various temperatures. The heat evolved in the precision oven system is difficult to accurately calibrate because the cells are air-cooled by forced convection whose patterns vary slightly between each set-up. However, relative measurements within a set are reproducible. There appears to be excess heat when comparing $\text{Heat}_{\text{GasIn}}$ vs. $\text{Heat}_{\text{GasOut}}$. The excess is about 10% of the total and may be a measurement error as the integrated temperature for the depressurization part of the cycle is less accurate because the heat evolves over a much longer period of time than the heat during pressurization and some baseline drift may occur. Note at 40°C the initial heat is not recovered in subsequent pressurization cycles because not all the deuterium is removed by just evacuating the sample. Therefore, subsequent pressurizations do not have the benefit from the heat of forming ZrD_x . The unit K-s/g is a derived unit related to energy.

4. Conclusions

Preparation of Pd–Zr–Pd via the route outlined by Arata et al. produced materials that were not very exothermic when exposed to hydrogen/deuterium. Modifying the procedure by heating at higher temperatures partially oxidized the alloys and allowed hydrogen/deuterium to absorb in an exothermic reaction but highly oxidized materials do not take-up hydrogen or deuterium. Measuring the weight gain during oxidation helps determine the oxidation state. By recording both the $\text{Heat}_{\text{GasIn}}$ and $\text{Heat}_{\text{GasOut}}$, cycling the materials, and using both hydrogen and deuterium, we found that the large amount of heat generated with these alloys is more consistent with known chemistry rather than invoking LENR. The small amount of heat unaccounted for (<10% of the total) is most likely unidentified chemistry or measurement error. Whether or not it is a new phenomenon that may be worth exploring cannot be definitively ruled-out from our results. It may be that the size of the Pd nano-particles in the matrix varies with preparation conditions and that a certain size of particles is required to allow LENR to occur. The size requirements and production processes to produce these particles (if that is important) still need to be delineated.

Acknowledgements

Funding from the Defense Threat Reduction Agency is gratefully acknowledged. We would like to thank Andrew Purdy for running the XRD spectra and David Knies for his assistance in the radiation measurements. The views, opinions, and/or findings contained in this manuscript are those of the authors and should not be interpreted as representing the official views or policies, either expressed or implied, of the Naval Research Laboratory or the Department of Defense. Approved for Public Release, Distribution Unlimited. NRL Security Release No. 11-1226-4344.

References

- [1] Shin-ichi Yamaura, Ken-ichiro Sasamori, Hisamichi Kimura, Akihisa Inoue, Yue Chang Zhang and Yoshiaki Arata, Hydrogen absorption of nanoscale Pd particles embedded in ZrO₂ matrix prepared from Zr–Pd amorphous alloys, *J. Mater. Res.*, **17** (2002) 1329–1334.
- [2] S. Yamaura, H. Kimura and A. Inoue, Hydrogen absorption of oxide composite materials prepared from melt-spun Zr–Pd–Ni alloys, Annual Fall Meeting of the Japan-Institute-of-Metals Location: Osaka, Japan, *Materials Trans.* **44** (2002) 696–699.
- [3] Yoshinori Arachi, Shuichi Emura, Akira Omura, Masanobu Nunogaki, Takeshi Asai, Shunichi Yamaura, Akihisa Inoue and Yoshiaki Arata, Structural analysis of nano-sized-Pd/ZrO₂ composite after H(D) absorption, *Solid State Ionics* **177** (2006) 1861–1864.
- [4] Yamazaki Toshimitsu, Sato Masaharu and Itoh Satoshi, Discovery of spontaneous deformation of Pd metal during hydrogen absorption/desorption cycles, *Proc. the Japan Academy Series B-Physical and Biological Sci.* **85** (2009) 183–186.
- [5] Y. Arata and Y.-C. Zhang, Development of ‘DS-Reactor’ as the practical reactor of ‘cold fusion’ based on the ‘DS-cell’ with ‘DS-cathode’, *Proc. ICCF12*, World Scientific, Singapore, 2006, pp. 44–54.
- [6] 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.
- [7] Y. Arata and Y. Zhang, The establishment of solid nuclear fusion reactor, *J. High Temperature Soc.* **34** (2008) 85–93 (in Japanese).
- [8] Akira Kitamura, Takayoshi Nohmi, Yu Sasaki, Akira Taniike, Akito Takahashi, Reiko Seto and Yushi Fujita, Anomalous effects in charging of Pd powders with high density hydrogen isotopes, *Phys. Lett.* **A373** (2009) 3109–3112.
- [9] Y. Sasaki, A. Kitamura, T. Nohmi, Y. Miyoshi and A. Taniike, Anomalous heat generation in charging of Pd powders with high density hydrogen isotopes (i) results of absorption experiments using Pd powders, presented in the *15th Int. Conf. on Condensed Matter Nucl. Sci.*, 2009, Rome, Italy.
- [10] A. Takahashi, A. Kitamura, Y. Sasaki, Y. Miyoshi, T. Nohmi, A. Taniike, R. Seto and Y. Fujita, Anomalous heat generation in charging of Pd powders with high density hydrogen isotopes (ii) discussions on experimental results and underlying physics, presented in the *15th Int. Conf. on Condensed Matter Nucl. Sci.*, 2009, Rome, Italy.
- [11] For Heat_{GasIn} (pressurization) and Heat_{GasOut} (depressurization or evacuation) the In/Out refers to the movement of the gas not the flow of heat, which is generally in the opposite direction.
- [12] P.L. Levine and K.E. Weale, The palladium + hydrogen equilibrium at high pressures and temperatures, *Trans. Faraday Soc.* **56** (1960) 357–362.
- [13] David A. Kidwell, Allison E. Rogers, Kenneth Grabowski and David Knies, Does gas loading produce anomalous heat? *15th Int. Conf. on Condensed Matter Nucl. Sci.*, Rome, Italy, October 5–9, 2009 (in Press).
- [14] D.A. Kidwell, D.L. Knies, A.E. Moser and D.D. Dominguez, Yes, virginia there is heat, but it is likely of chemical origin, *9th Int. Workshop on Anomalies in Hydrogen/Deuterium Loaded Metals*, Certosa di Pontignano in Siena, Italy, 17–19 September 2010.
- [15] Sheng-Yang Huang, Chin-Da Huang, Boh-Tze Chang and Chuin-Tih Yeh, Chemical activity of palladium clusters: sorption of hydrogen, *J. Phys. Chem. B* **110** (2006) 21783–21787.
- [16] Shu-Chin Chou, Shu-Hui Lin and Chuin-Tih Yeh, Isothermic heat of sorption of dihydrogen on alumina-supported palladium, *J. Chem. Soc. Faraday Trans.* **91** (1995) 949–951.
- [17] L.F. Chen, J.A. Wang, M.A. Valenzuela, X. Bokhimi, D.R. Acosta, and O. Novaroc, Hydrogen spillover and structural defects in a PdO/zirconia nanophase synthesized through a surfactant-templated route, *J. Alloys Compounds* **417** (2006) 220–223.
- [18] Often a control for spillover is testing the support without a catalyst present and generally the support does not absorb hydrogen. This is problematic because a catalyst is required to activate the hydrogen for spillover to occur. Other measurements such as the uptake vs. pressure are also problematic because both spillover and absorption into the particles can occur at similar rates. Thus, there are no good techniques for measuring Pd:H ratios on supported nanoparticles.
- [19] Pen Chou and M.A. Vannice, Calorimetric Heat of Adsorption Measurements on Palladium I. Influence of Crystallite Size and Support on Hydrogen Adsorption, *J. Catalysis* **104** (1987) 1–16.
- [20] Pen Chou and M.A. Vannice, Calorimetric Heat of adsorption measurements on palladium I. Influence of crystallite size and support on hydrogen adsorption II. Influence of crystallite size and support on CO adsorption, *J. Catalysis* **104** (1987) 17–30.

- [21] P. Dantzer, W. Luo, T.B. Flanagan and J.D. Clewley, Calorimetrically measured enthalpies for the reaction of h(g) with Zr and Zr alloys, *Metallurgical and Materials Trans. A* **24** (1993)1471–1479.
- [22] Y. Arata, Y.C. Zhang and X.F. Wang, Production of helium and energy in the solid fusion, presented at the *15th Int. Conf. on Condensed Matter Nucl. Sci.* 2009, Rome, Italy, S4–01.
- [23] Kitamura et al., Measure about 2.3 kJ/g of Zr_{65.4}–Pd_{34.6}. Formation of ZrH_{1.5} would produce about 0.9 kJ/g, formation of PdH_{0.7} would produce about 0.12 kJ/g and reduction of PdO would yield 0.65 kJ/g. These reactions total to 1.67 kJ/g, much lower than that measured. Some other reaction must be occurring to produce the measured heat, which may bear investigating.