J. Condensed Matter Nucl. Sci. 38 (2024) 96–107

Research Article

Estimation of the Heat Generation of the Metal Composite Powder Absorbing the Pulsed Flow of Hydrogen Gas

Tomotaka Kobayashi, Ken Naitoh, Daiki Okada, Ryuki Nakagawa, and Yuta Toba
Faculty of Science and Engineering, Waseda University, Tokyo, Japan

Masaharu Uchiumi and Daisuke Nakata
Muroran Institute of Technology, Hokkaido, Japan

Abstract

Anomalous heat generation during the exposure of nickel or palladium powder to hydrogen or deuterium gas injected with pulse flow is reported here. In our previous report in ICCF23, a temperature rise of about 10 K was observed after the absorption of 0.5 MPa hydrogen gas by Pd-Ni-Zr composite powder at 244 °C. In these tests hydrogen gas was injected slowly. In this research, we added a solenoid valve to our reaction system with a small chamber, and we conducted a hydrogen gas absorption experiment with pulsed flow generated by a solenoid valve, up to 295 °C and 5 MPa. As a result, a temperature rise of over 100 K was observed. We also estimated the energy generated in the experiments. As a result, the heat release rate estimated is about 30 W, for a very small reaction chamber with only 3 g of Pd-Ni-Zr composite powder, even though we have done experiments during a very short period of fewer than ten minutes for absorption. The result indicates that the pulsed flow of hydrogen gas increases the amount of heat generation.

Keywords: anomalous heat, gas absorption, estimation, pulse flow

1. Introduction

Anomalous heat generation from the exposure of nickel or palladium powder to hydrogen or deuterium gas were reported in previous papers [1]–[2]. It was also reported that anomalous effects occur when mixed oxides of Pd and Zr absorb hydrogen (or deuterium) gas [3].

We have focused on anomalous heat generation in hydrogen (or deuterium) gas absorption at higher pressure conditions, using the metal composite powder reported in previous research. In our previous report [4], we developed a small constant-volume reaction system (shown in Fig. 1) and conducted fundamental experiments of anomalous heat generation with hydrogen gas absorption. To inject hydrogen gas gradually (slowly), a hand-operated valve is included between the safety valve and the gas supply device. In the experiments, about 10 K ΔT temperature rise was observed

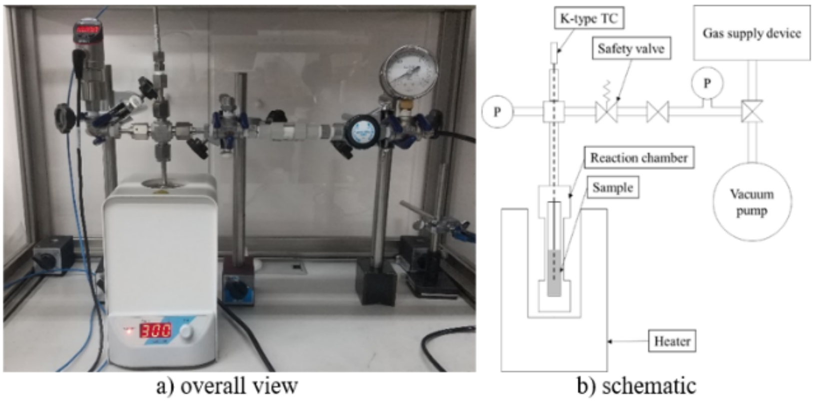

Figure 1. Reaction system developed in our previous report [4].

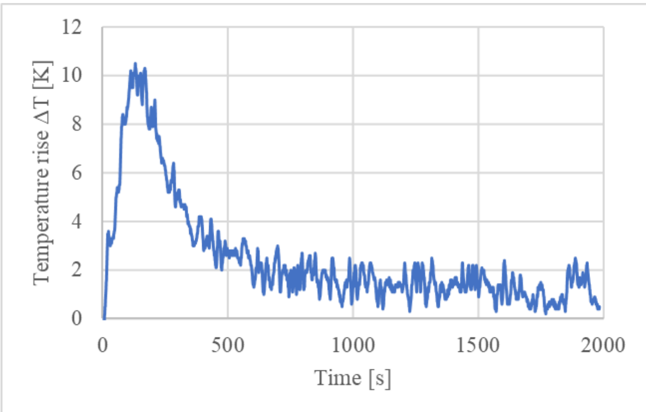

Figure 2. Experimental result in our previous report [4].

with the absorption of 0.5 MPa hydrogen gas by Pd-Ni-Zr composite powder (PNZ10r, provided by Technova Inc.) [5] at 244 °C (Fig. 2).

In this report, we added a solenoid valve to generate a pulse flow of hydrogen gas into the reaction chamber (Fig. 3). We conducted experiments on anomalous heat generation during hydrogen gas absorption. Our goal was to confirm whether the collision of the pulse jet flow on the PNZ powder surface produces increased pressure and temperature [6], which may lead to more anomalous heat generation. We also estimate the energy generated in the experiments, based on how much the sample temperature increases.

2. Experimental Device

Figure 4 shows a schematic of the reaction system. The reaction system consists of a heater, reaction chamber, K-type thermocouple, gas supply device, two pressure gauges, solenoid valve, hand valve, three-way valve, vacuum pump, and a safety valve.

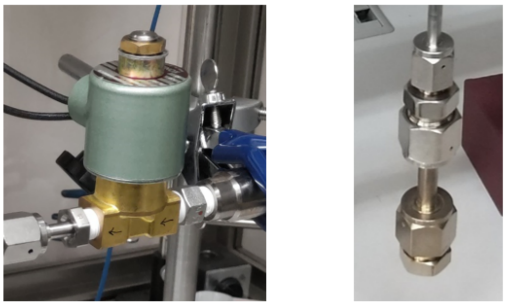

Figure 3. Details of reaction chamber system and a solenoid valve in this report.

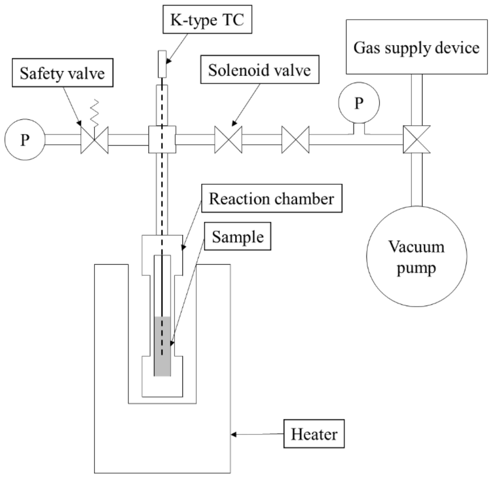

Figure 4. Schematic of the reaction system.

The reaction chamber volume is about 2 mL. The chamber is made of stainless steel (SUS316L). The heater (GBSD-300, As One Corporation) was used to preheat the reaction chamber to a range of 100 - 300 °C. The space between the heater and the reaction chamber is filled with glass beads. The K-type thermocouple (HTK0227, Hakko Electric Co., Ltd.), whose tip is embedded in the sample, is used to measure the sample temperature. The gas supply device provides hydrogen (or nitrogen) gas (1.0 MPa maximum) while performing experiments. (In experiment No. 5, a high-pressure hydrogen gas tank was used instead). The pressure of gas in the reaction chamber and the pressure of gas source are measured by two pressure gauges. In the experiments, the solenoid valve makes a pulse flow of hydrogen gas, and the hand valve regulates its flow rate. The three-way valve is used for switching gas loading and evacuation. The scroll pump (ISP-250C, Anest Iwata Corporation) is used for evacuation. The ultimate pressure (the lowest pressure that can be reached within a realistic evacuation time) of the vacuum pump is 1.6 Pa. The safety valve (RAT2V-1000, IBS Inc.) is installed to avoid fracturing the reaction chamber. The safety valve opens when the pressure in the reaction chamber exceeds 1.0 MPaG (In experiment No. 5, a relief valve that allowed up to 10 MPaG of pressure was used instead.)

Table 1. Specifications of the reaction system.

Material of reaction chamber	SUS316L
Volume of reaction chamber	2 mL
Reaction chamber internal diameter	7.40 mm
Reaction chamber external diameter	9.52 mm
Height occupied by the sample	30.6 mm
Ultimate pressure of vacuum pump	1.6 Pa
Maximum pressure of loading gas	1.0 MPa (5 MPa at experiment No. 5)
Maximum temperature of heater	300 °C
Cracking pressure of relief valve	1.0 MPaG (10 MPaG at experiment No. 5)

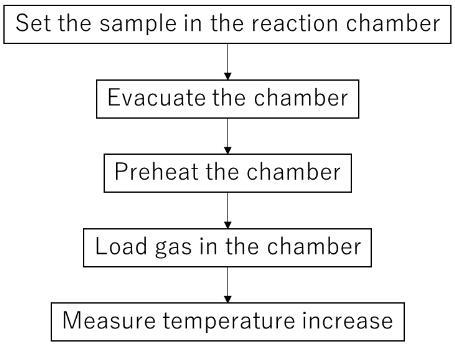

Figure 5. Experimental procedure.

Specifications of the reaction system are shown in Table 1.

3. Experimental Procedure

The experimental procedure is shown in Fig. 5. First, the sample of Pd-Ni-Zr composite powder, (designated PNZ10r [5]) is placed in the reaction chamber. Then, the reaction chamber is evacuated with the vacuum pump. After that, the chamber is preheated with the heater. After the preheating, hydrogen gas (or nitrogen gas for a control experiment) is loaded to the upstream side of the solenoid valve. The solenoid valve then opens, and the pulse flow of hydrogen (or nitrogen) gas enters the chamber (Fig. 6). A temperature increase of the sample is measured by the K-type thermocouple. At the end of the experiment, the chamber is evacuated again, so as not to leave the loaded gas in it.

4. Results

4.1. Experimental Conditions

Experimental conditions are shown in Table 2. In experiments, 3.0 g of Pd-Ni-Zr composite powder (PNZ10r, provided by Technova Inc.) [5] was used as a sample. Experiments were conducted using hydrogen gas, and nitrogen gas as the control experiment. (The control experiment using nitrogen gas is done before using hydrogen gas.) The experiments were conducted in the range of gas pressure 0.12 - 5 MPa, and initial temperature of sample 95 - 295 °C.

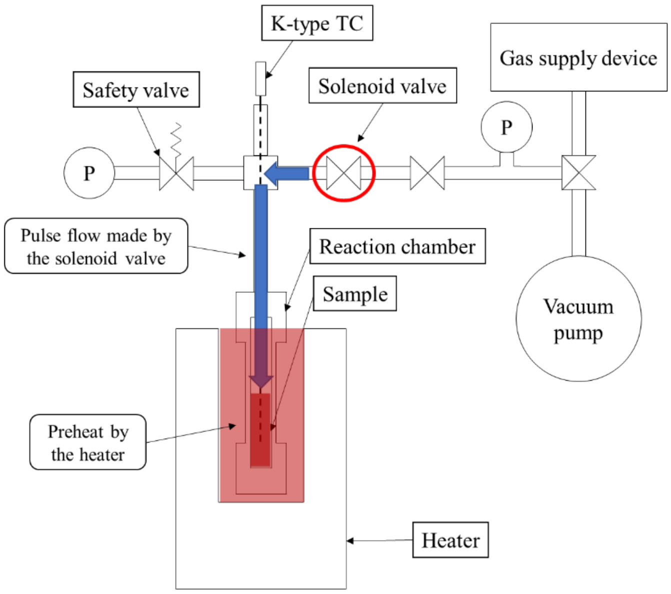

Figure 6. Schematic of the latest experiment, with pulse flow valve and preheating added.

Table 2. Experimental conditions.

Sample	Pd-Ni-Zr composite powder
Sample mass	3.0 g
Kind of gas	Hydrogen or Nitrogen (control experiment)
Gas pressure	0.12 - 5 MPa
Initial temperature	95 - 295 °C

4.2. Method of Estimating Energy

In this report, we roughly estimated the energy generated in the experiments. For simplicity, three assumptions are made for the estimate.

1. The sample temperature is uniform during the experiment.
2. The sample and the chamber absorb the generated heat.
3. The temperature on the outer surface of the chamber is the same as the sample temperature.

First, the heat absorption by the sample is considered. According to assumption 1, the heat amount absorbed by the sample Q_{sample} is calculated from Eq. 1.

$$Q_{\text{sample}}\,[J] = \Delta T_{\max}\,[K] \times C_{\text{sample}}[J/K] \tag{1}$$

where $\Delta T_{\max}$ denotes the maximum temperature rise in the experiment and C_{sample} $(= 1.38\ [J/K])$ denotes the heat capacity of the sample.

Next, the heat absorbed by the reaction chamber is considered. To simplify, it is assumed that the temperature distribution in the reaction chamber wall is uniform and equals the temperature in the powder because the time constant of the wall is small compared to the time constant of the powder.

Table 3. Results of the experiments without pulse flow.

No.	Sample	Gas pressure	Initial temp.	Temp. rise	Heat generation	
1	Pd-Ni-Zr 3.0 g	0.12 MPa	95 °C	1.2 K	5.47 J	0.01 W
2	Pd-Ni-Zr 3.0 g	0.9 MPa	240 °C	12.4 K	56.5 J	0.72 W

Table 4. Results of the experiments with pulse flow.

No.	Sample	Gas pressure	Initial temp.	Temp. rise	Heat generation	
3	Pd-Ni-Zr 3.0 g	0.12 MPa	95 °C	9.1 K	41.5 J	1.06 W
4	Pd-Ni-Zr 3.0 g	0.9 MPa	240 °C	35.0 K	159 J	17.7 W
5	Pd-Ni-Zr 3.0 g	5 MPa	295 °C	115 K	524 J	105 W

As a further simplification we assume that the heat loss through the insulation is negligible. According to assumption 3, the heat amount absorbed by the chamber wall Q_{wall} is calculated from Eq. 2.

$$Q_{\mathrm{wall}}\,[J] = \Delta T_{\max}\,[K] \times C_{\mathrm{wall}}[J/K] \tag{2}$$

where $C_{\mathrm{wall}}\,(= 3.17\;[J/K])$ denotes the heat capacity of the chamber wall.

Thus, the energy is estimated from Eqs. 3 and 4 derived from the above assumptions.

$$Q\,[J] = Q_{\mathrm{sample}} + Q_{\mathrm{wall}} \tag{3}$$

$$P\,[W] = Q\,[J]/t[s] \tag{4}$$

where t denotes the time from the start of the experiments to the sample temperature becoming maximum.

4.3. Summary of Experimental Results for Heat Release Rates

Table 3 shows the results and conditions of the experiments without pulse flow, whereas Table 4 shows results from the experiments with pulse flow.

To bolster these results, let us assume that only the center of the sample is $\Delta T_{\max}$, the adiabatic assumption is close to the true condition, so in that case we should assume that the sample absorbs all the generated heat. In this case, Q is calculated using only Eq. 1 and the estimated heat is 159 J in experiment No. 5. The true value of generated heat is somewhere in between those.

4.4. Details of Experimental Data for Conditions No. 1 and No. 3 (Pd-Ni-Zr 3.0 g, 95 °C, 0.12 MPa)

In Fig. 7 in condition No. 1 without the pulse flow, time-dependent experimental temperatures are demonstrated with 3.0 g of Pd-Ni-Zr composite powder, 0.12 MPa of gas pressure, and 95 °C initial temperature. In Fig. 7, the orange line is for nitrogen gas loaded, whereas the blue line is for hydrogen gas. Figure 8 shows the temperature rise from the control experiment with nitrogen gas, i.e., the temperature difference between cases of hydrogen and nitrogen. In this experiment, the temperature rise begins just after hydrogen gas loading. However, there is no obvious difference from the control experiment. The estimated energy and power generated in the experiment are very small, 5.47 J and 0.01 W.

In Fig. 9 in condition No. 3 with the pulse flow, time-dependent experimental temperatures are demonstrated with 3.0 g of Pd-Ni-Zr composite powder, 0.12 MPa of gas pressure, and 95 °C initial temperature. The orange line shows results for nitrogen gas, and the blue line for hydrogen gas. Figure 10 shows the temperature difference between cases of hydrogen and nitrogen.

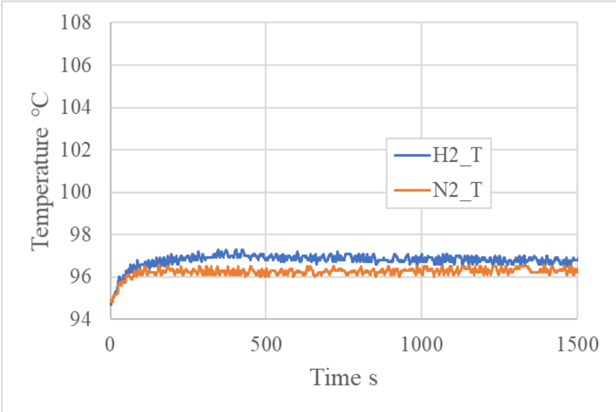

Figure 7. Result of the experiment (No. 1) [7].

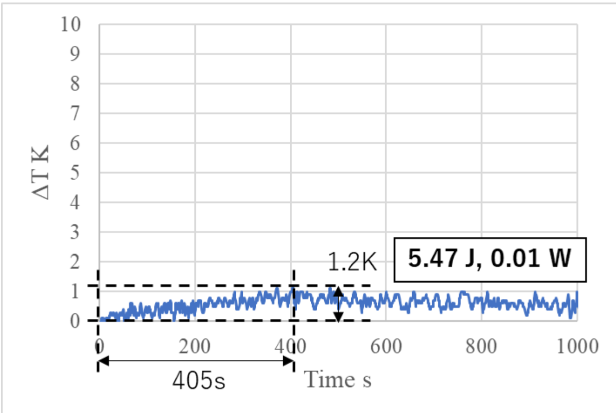

Figure 8. Temperature rise ΔT with estimation of heat generation (No. 1).

A temperature rise of 9.1 K is observed 39 seconds after the beginning. The estimated energy and power generated in the experiment are 41.5 J and 1.06 W.

A larger temperature rise and more heat generation rate for Condition No. 3, pushed by pulse flow, are observed in comparison with No. 1 having no pulse flow, while Condition No. 3 shows earlier timing of the largest temperature.

4.5. Details of Experimental Data for Conditions No. 2 and No. 4 (Pd-Ni-Zr 3.0 g, 240 °C, 0.9 MPa)

In our recent experiments we increased the initial pressure of the hydrogen gas. In Fig. 11, in condition No. 2, without the pulse flow, time-dependent experimental temperatures are demonstrated with 3.0 g of Pd-Ni-Zr composite powder, 0.9 MPa of gas pressure, and 240 °C initial temperature. Figure 12 shows the temperature rise from the control experiment for nitrogen gas, i.e., the temperature difference between the cases of hydrogen and nitrogen. A temperature

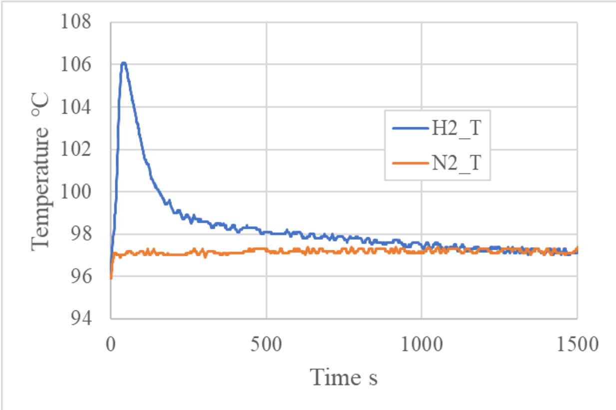

Figure 9. Result of the experiment (No. 3) [7].

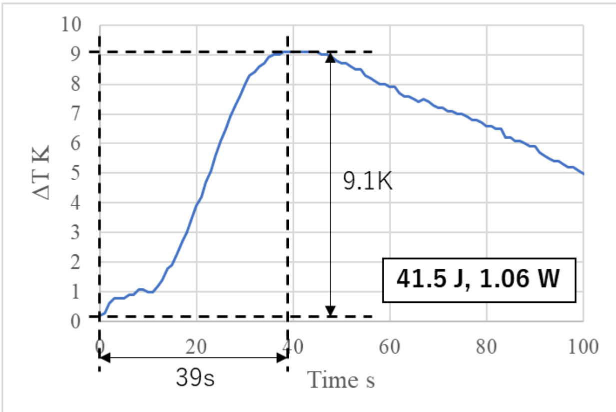

Figure 10. Temperature rise ΔT with estimation of heat generation (No. 3).

rise of 12.4 K of temperature rise is observed 79 seconds after beginning. The estimated energy and power generated in the experiment are 56.5 J and 0.72 W.

In Fig. 13 in condition No. 4 with the pulse flow, time-dependent experimental temperatures are demonstrated with 3.0 g of Pd-Ni-Zr composite powder, 0.9 MPa of gas pressure, and 240 °C initial temperature. Figure 14 shows the temperature difference between cases of hydrogen and nitrogen. A temperature rise of 35.0 K is observed 9 seconds after the test begins. The estimated energy and power generated in the experiment are 159 J and 17.7 W.

It is stressed that the higher pressure of hydrogen gas brings larger temperature gain due to absorption.

4.6. Details of Experimental Data for Condition No. 5 (Pd-Ni-Zr 3.0 g, 295 °C, 5 MPa, with the Pulse Flow)

In Figs. 15 and 16 at condition No. 5 with the pulse flow, time-dependent experimental temperatures are demonstrated with 3.0 g of Pd-Ni-Zr composite powder, 5 MPa of gas pressure, and the initial temperature of 295 °C. In Fig. 15,

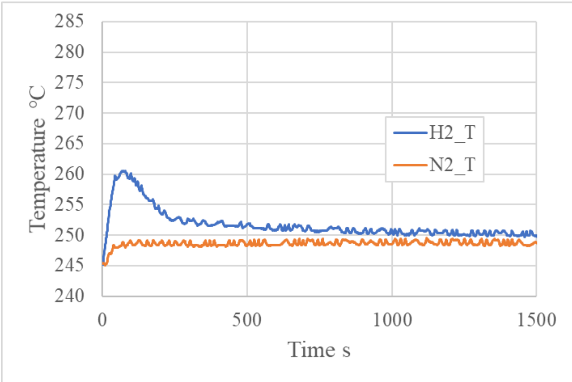

Figure 11. Result of the experiment (No. 2) [7].

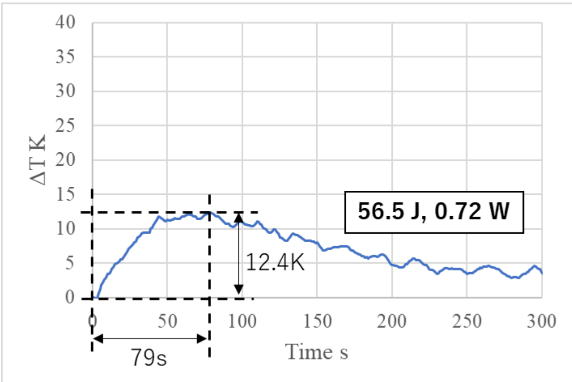

Figure 12. Temperature rise ΔT with estimation of heat generation (No. 2).

a yellow line shows the time history of the pressure in the reaction chamber, and the blue line shows the time history of the sample temperature. The temperature rise begins just after hydrogen gas loading. After the temperature rise begins, it increases by 115 K in 5 seconds. The estimated energy and power generated in the experiment are 524 J and 105 W (In this experiment, the control experiment with nitrogen gas was not conducted. Energy is estimated from the temperature rise from the start of the experiment and the time to reach the maximum temperature.)

Because we have no control experiment with nitrogen gas for this test, we had to carefully calibrate the measured value of temperature rise to estimate the heat accurately. When hydrogen gas is loaded in the chamber without the sample, a temperature rise of about 20 K is observed. From this, the actual temperature rise with the sample is estimated to be 95 K. In this case, the estimated energy and power generated in the experiment are 433 J and 86.6 W.

It should be noted that the estimated heat generation in this experiment is much larger than the predicted heat generation by a chemical reaction. The principal exothermic chemical reactions are palladium hydration and hydrogen oxidation. (In this experiment, zirconium oxide cannot be reduced by hydrogen, and nickel oxide is hardly reduced.)

First, the heat generated by the palladium hydration is predicted to be about 20 J at most (assuming the palladium absorbs hydrogen until H / Pd = 1). The 3.0 g of the sample contains about 0.1 g of palladium [5] and the heat release by

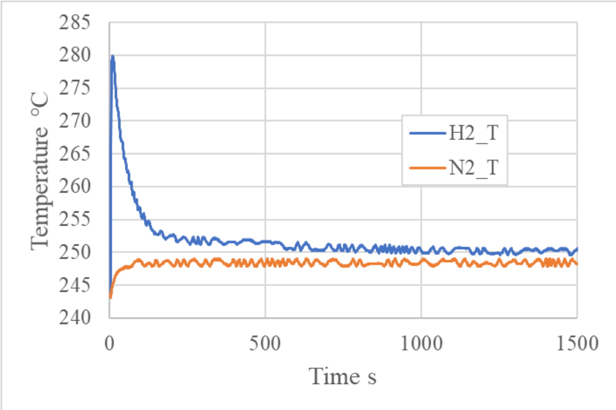

Figure 13. Result of the experiment (No. 4) [7].

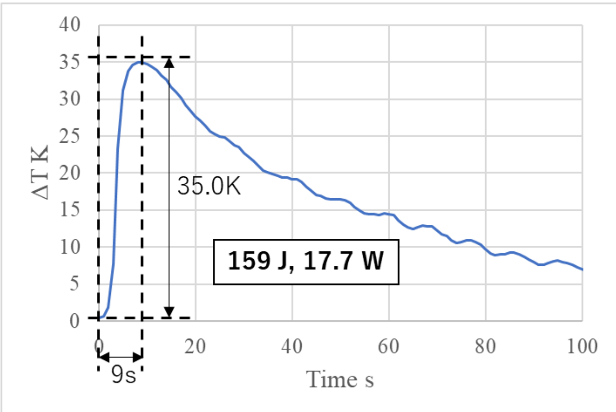

Figure 14. Temperature rise ΔT with estimation of heat generation (No. 4).

palladium hydration is 19.1 kJ/mol H [8]. On the other hand, the heat generated by the hydrogen oxidation is predicted about 3 J at most (assuming 1 kPa of air remains when the hydrogen gas is loaded), where the heat generation by hydrogen oxidation is 241.83 kJ/mol O [9] and the inner volume of the reaction system (including reaction chamber and the surrounding pipes) is about 50 mL. Even the sum of the maximum heat generation of these reactions (about 23 J) is much smaller than the estimated energy generated in the experiment (433 J). This result may show the anomalous heat generation that occurred in experiment No. 5 (Pd-Ni-Zr 3.0 g, 295 °C, 5 MPa, with the pulse flow). In the near future, we plan to conduct further experiments and improve measurement (and estimation) accuracy to ascertain what the heat generation observed in the experiment consists of.

In addition, these results may show that heat generation in the hydrogen gas absorption by the Pd-Ni-Zr sample has a positive pressure dependence. While the sample temperature is higher than the heater temperature, outward heat flow occurs. However, the estimated heat flux is about 0.7 W at maximum (where the temperature rise is 115 K), assuming the heat transfer from the reaction chamber (9.52 mm diameter × 30.6 mm high cylinder) to the heater. (Our method

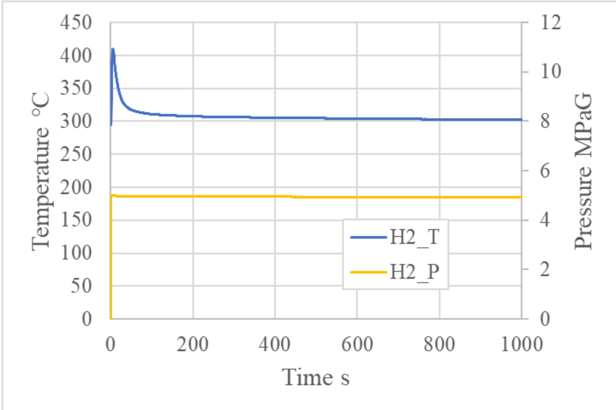

Figure 15. Result of the experiment (No. 5).

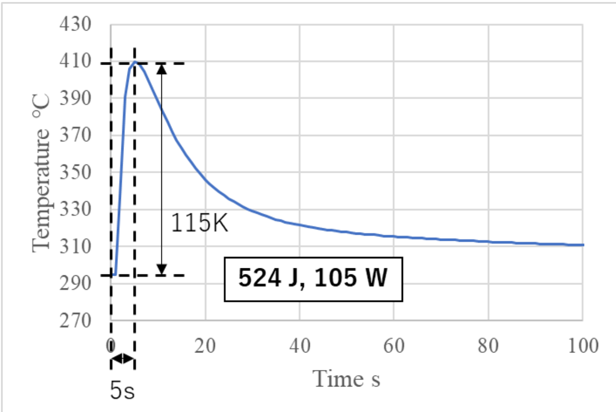

Figure 16. Estimation of heat generation (No. 5).

of estimating the heat transfer is described in section 4.2). Thus, it can be said that heat generation in the experiment has a positive pressure dependence.

5. Conclusion

We first conducted experiments on anomalous heat generation in hydrogen gas absorption with the pulse flow of hydrogen gas to confirm the effect of the pulse flow on anomalous heat generation, while with higher pressures of hydrogen gas loaded. The results obtained show that the pulse flow and higher-pressure conditions produce more heat in hydrogen gas absorption by Pd-Ni-Zr composite powder.

Next, we also tested at a very high-pressure condition of about 5 MPa, which leads to a much larger heat release of about 524 J. This is also larger than the maximum heat generation from a chemical reaction (23 J). This result apparently shows anomalous heat generation occurred in the experiment. In the near future, we will conduct further experiments and improve measurement (and estimation) accuracy to ascertain what the heat generation observed in the experiment consists of.

Credit Authorship Contribution Statement

Mr. Tomotaka Kobayashi and Prof. Dr. Ken Naitoh mainly executed the plans, theoretical and computational studies, developments of constant chamber reactors, and their experiments at Waseda University and the Shiraoi engine test research center of Muroran Institute of Technology. Prof. Dr. Masaharu Uchiumi, Prof. Dr. Daisuke Nakata, and Mr. Tomoyuki Takano made important contributions to the setup and operation of experiments with heat generation due to high-pressure hydrogen gas and metal particles at nanometer size in constant-volume chamber, at the Shiraoi engine test research center of Muroran Institute of Technology.

Acknowledgements

This work was supported by Grant-in-Aid for JSPS Fellows (21J21973) and the grant of The Thermal & Electric Energy Technology Foundation (TEET). The experiments on anomalous heat generation in hydrogen gas absorption at higher than 1 MPa were performed at Shiraoi engine test research center of the Muroran Institute of Technology with Pd-Ni-Zr composite powder made by Technova Inc. We appreciate Technova Inc. for the useful discussion and for providing the sample of Pd-Ni-Zr powder. Sincere thanks are also due to the other members of the Naitoh Laboratory for their help.

References

[1] A.G. Parkhomov, V.A. Zhigalov, S.N. Zabavin, A.G. Sobolev, T.R. Timerbulatov, "Nickel-hydrogen heat generator continuously working for 7 months," *22nd International Conference on Condensed Matter Nuclear Science (ICCF22) Book of Abstracts*, Assisi, p. 77, 2019.

[2] Y. Arata, Y. Zhang, "The Establishment of Solid Nuclear Fusion Reactor," *J. High Temp. Soc.*, vol. 34, pp. 85–93, 2008.

[3] Kitamura, A., Nohmi, T., Sasaki, Y., Taniike, A., Takahashi, A., Seto, R., & Fujita, Y. (2009). Anomalous effects in charging of Pd powders with high density hydrogen isotopes. *Physics Letters A, 373*(35), 3109–3112. https://doi.org/10.1016/j.physleta.2009.06.061

[4] T. Kobayashi, J. Shigemura, K. Naitoh, Y. Mori, R. Seto, J. Hachisuka, "Temperature and pressure dependence of anomalous heat generation occurring in hydrogen gas absorption by metal powder," *J. Condensed Matter Nucl. Sci.* vol. 36, pp. 318–326, 2022.

[5] A. Takahashi, H. Ido, A. Hattori, R. Seto, et al., "Latest Progress in Research on AHE and Circumstantial Nuclear Evidence by Interaction of Nano-Metal and H(D)-Gas", *J. Condensed Matter Nucl. Sci.*, vol. 33, pp. 14–32, 2020.

[6] Konagaya, R., Naitoh, K., Kobayashi, T., Isshiki, Y. et al., "Two Prototype Engines with Colliding and Compression of Pulsed Supermulti-Jets through a Focusing Process, Leading to Nearly Complete Air Insulation and Relatively Silent High Compression for Automobiles, Motorcycles, Aircrafts, and Rockets," SAE Technical Paper 2020-01-0837, 2020, https://doi.org/10.4271/2020-01-0837.

[7] T. Kobayashi, K. Naitoh, J. Shigemura, D. Okada, Y. Nomura, "Heat generation of metal composite powder caused by the pulse flow of hydrogen gas," *Proceedings of the* 22^{nd} *Meeting of Japan CF Research Society JCF 22*, pp. 40–49, 2022.

[8] T. B. Flanagan, W. Luo, and J. D. Clewley, "Calorimetric enthalpies of absorption and desorption of protium and deuterium by palladium," *Journal of the Less-Common Metals*, 172–144, pp. 42–55, 1991.

[9] Chase, M.W., Jr., NIST-JANAF Themochemical Tables, Fourth Edition, J. Phys. Chem. Ref. Data, Monograph 9, 1998, 1–1951.