Hydrogen isotope absorption/adsorption characteristics of Ni·Pd binary nano-particles

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Abstract. A twin absorption system has been used for experiments on D_2 and H_2 gas absorption of the oxide nano-composites of Pd, Ni and Zr. The sample powders used in the present work are Ni·Pd binary nanoparticles dispersed in ZrO_2 holder-flakes (PNZ2B) which were provided by B. Ahern. The observed loading ratio and the specific heat release in the first phase of as-received PNZ2B sample runs were both very large. The large heat release could include energy of oxygen pickup reaction as well as that of hydrogen isotope absorption. To investigate the effect of oxidization on absorption rate and heat release rate, we compared runs with the sample after forced deoxidization and the sample after forced oxidization to control oxygen amount. We have observed the time-dependent absorption energy per a D atom, η_D, showing sometimes much larger values than η_H, which could suggest existence of heat component of nuclear origin.

Keywords:Pd-Ni-Zr nano-powder, Deuterium absorption, D/Pd·Ni

1. Introduction

Arata and Zhang reported heat and ^{4}He generation by deuterium (D) absorption in nano-sized Pd·Ni·Zr powders [1]. To investigate this phenomenon quantitatively, we constructed a twin absorption system for D_2 or H_2 gas absorption which can make mass-flow-calorimetry [2]. We used commercially available samples and those supplied by Santoku Corporation [3,4].

On the other hand, B. Ahern (B.A.) fabricated his own samples and measured temperature and pressure during gas absorption experiment. He reported very large loading ratio of hydrogen and heat evolution [5]. We offered him to examine the heat release and absorption characteristics with our twin-absorption system. This report describes the results of time-dependent measurements of hydrogen isotope gas absorption / adsorption and associated heat evolution from the Pd·Ni·Zr oxide nano-compounds supplied by B.A.

2. Experimental apparatus

Composition of the PNZ2B sample is Pd (4%), Ni (29%) and Zr (67%). We used a twin absorption system consisting of two equivalent chambers for hydrogen isotope gas absorption / adsorption experiments, one of which is shown schematically in Fig. 1. Pd nano-particles are put in the reaction chamber, and the outer chamber is evacuated for thermal insulation during hydrogen isotope absorption / adsorption. The reservoir tank is filled with D_2 (H_2) gas at a pressure of 0.4 MPa, typically, before an absorption run starts. The flow rate of D_2 (or H_2) gas is adjusted and regulated with a "Super Needle" valve.

Sheath heaters with resistance of 110.0 Ω in A1 and 36.1 Ω in A2 are used for sample baking,

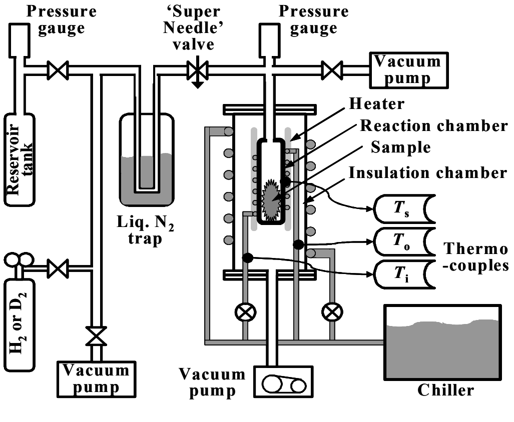

Fig. 1. Schematic of one-part of the twin system.

and also for sample heating in the cases of forced deoxidization and forced oxidization. Alumel-chromel thermo-couples are used to measure temperatures.

For calorimetry, the coolant water is maintained constant (±0.1 °C) at near-room temperature with a chiller, and the flow rate is controlled with a digital coolant transmitter at a rate of 6 cc/min, which recovers heat with an efficiency of 63.1 ±5.8 %. There is a delay in the response of the temperature difference due to the indicial response with a time constant of 5.2 minutes. Calorific power is calculated from temperature difference between the exit and the entrance of water-coolant. The calibrated conversion factor is 0.67 W/K.

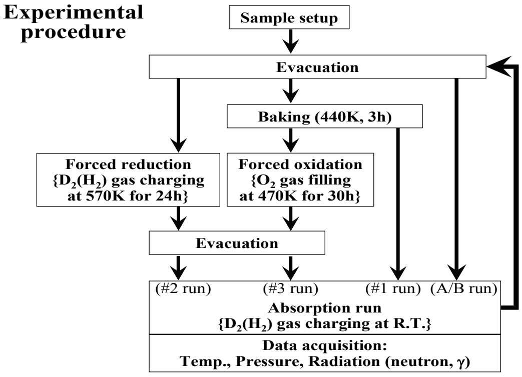

Fig.2. Flow-chart of the experimental procedure.

Table 1. Nomenclature for the run number.

#1	**absorption run using a virgin sample**
#2	**absorption run after forced de-oxidization**
#3	**absorption run after forced oxidization**
#nA	**absorption run following #n without baking**
#nB	**absorption run following #nA without baking**
#n(N)d	**desorption run by evacuation aftyer the absorption run #n(N)**

3. Experimental procedure

Figure 2 shows the experimental procedure. The run number expresses the conditions of the sample used in the run, using the letters defined in Table 1. The as-received sample is baked at 440 K for 2 hours in vacuum, and subjected to the D_2 (H_2) absorption run (#1 run). The sample is reused either without any treatment (A or B run) or after the specified treatment; forced deoxidization (#2 run) or forced oxidization (#3 run).

In the case of forced deoxidization, the sample is heated after filling the reaction chamber with the hydrogen isotope gas at a pressure of 0.3 MPa, and kept at 570 K for 24 hours. On the other hand, in the case of forced oxidization, the sample is treated in the similar manner using oxygen gas at a pressure of 0.4 MPa kept at 470 K or 570 K for 30 hours. The fraction of oxidized atoms, PdO and NiO, is calculated from the pressure drop during this procedure.

In the #3 run of the oxidized sample, the released heat includes energy of oxygen pickup reaction, Q_{red} eV/atom-O, and that of hydrogen isotope absorption / adsorption, the 'hydridation' energy, $Q_{\mathrm{D(H)}}$ eV/atom-D(H);

$$\mathrm{Pd(Ni)O}_x + \left(x + \frac{y}{2} \right) \mathrm{D}_2 = x\mathrm{D}_2\mathrm{O} + \mathrm{Pd(Ni)D}_y \,, \quad + xQ_{\mathrm{red}} + yQ_{\mathrm{D}}$$

$$\mathrm{Pd(Ni)O}_x + \left(x + \frac{y}{2} \right) \mathrm{H}_2 = x\mathrm{H}_2\mathrm{O} + \mathrm{Pd(Ni)H}_y \,. \quad + xQ_{\mathrm{red}} + yQ_{\mathrm{H}} \qquad \text{(1D,1H)}$$

where x is the fraction of Pd (Ni) atoms oxidized, and y is the fraction of Pd (Ni) atoms hydrized. The total energy released is expressed as E_1;

$$E_1 = xQ_{\mathrm{red}} + yQ_{\mathrm{D(H)}} \qquad (2)$$

The energies of formation of oxides associated in the present phenomena are as follows;

$$\mathrm{Pd} + \frac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{PdO} + 0.886\,\mathrm{eV}, \qquad (3)$$

$$\mathrm{Ni} + \frac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{NiO} + 2.478\,\mathrm{eV}, \qquad (4)$$

$$\mathrm{D}_2 + \frac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{D}_2\mathrm{O} + 2.654\,\mathrm{eV}, \qquad (5\mathrm{D})$$

$$\mathrm{H}_2 + \frac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{H}_2\mathrm{O} + 2.511\,\mathrm{eV}, \qquad (5\mathrm{H})$$

The energies of the oxygen pickup reactions, Q_{red}, are calculated by combining the above equations;

$$\mathrm{PdO} + \mathrm{D}_2 \rightarrow \mathrm{Pd} + \mathrm{D}_2\mathrm{O} + 1.768\,\mathrm{eV} \qquad (6\mathrm{D})$$

$$\mathrm{PdO} + \mathrm{H}_2 \rightarrow \mathrm{Pd} + \mathrm{H}_2\mathrm{O} + 1.625\,\mathrm{eV} \qquad (6\mathrm{H})$$

$$\mathrm{NiO} + \mathrm{D}_2 \rightarrow \mathrm{Ni} + \mathrm{D}_2\mathrm{O} + 0.176\,\mathrm{eV} \qquad (7\mathrm{D})$$

$$\mathrm{NiO} + \mathrm{H}_2 \rightarrow \mathrm{Ni} + \mathrm{H}_2\mathrm{O} + 0.033\,\mathrm{eV} \qquad (7\mathrm{H})$$

The energies of the oxygen pickup reactions for PdO, Eqs. (6D) and (6H), are much larger than those for NiO, eqs. (7D) and (7H).

We use Eq. (2) to know the value of $Q_{\mathrm{D(H)}}$ by subtracting the first term xQ_{red} from the experimentally obtained value of E_1. However, we don't know the fractions of PdO and NiO. The purpose of the present study is to show that $Q_{\mathrm{D(H)}}$ is much larger than the value obtained so far for the bulk samples. Therefore, underestimation of Q_{red} must be avoided not to overestimate $Q_{\mathrm{D(H)}}$. We then assumed here that there were no NiO having the smaller Q_{red}, and that Q_{red} = 1.77 eV for D_2 and Q_{red} = 1.63 eV for H_2 for conservative estimation.

4. Results of experiments

Figure 3 shows typical variation of the heat output, W_{D} and W_{H}, pressure in the reaction chamber, P_{D} and P_{H}, and the loading ratio, L_{D} and L_{H}, in the hydrogen isotope absorption run for as-received samples, PNZ2B1 and PNZ2B2. The maximum output powers of 0.4 W and 0.2 W, respectively, are modest, but the heat release lasts for more than 1000 minutes.

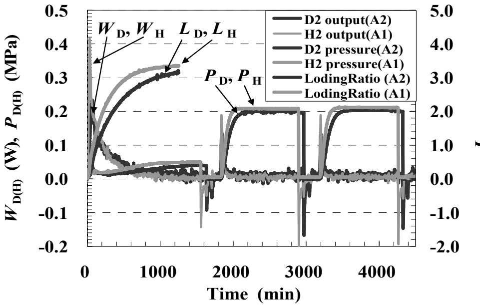

Fig. 3. Evolution of heat, pressure in the reaction chamber after introduction of D_2 (or H_2) gas and the time-dependent loading ratio (H-PNZ2B1#1 and D-PNZ2B2#1).

The samples show peculiar pressure changes in the early stage of the #1 run. Figure 4 shows the relation between the pressure and the loading ratio for the PNZ2B1 and PNZ2B2 samples. The gas absorption / adsorption does not start until the pressure is increased to some value. This behavior of the pressure was never observed for samples containing no NiO [4].

It seems to suggest the following mechanism: The surface NiO layer is relatively hard to deoxidize. However, once the deoxidization reaction (7D) or (7H) is initiated at a point to expose metallic Ni to D_2 / H_2 atmosphere, rapid dissociation to D / H atoms and adsorption followed by rushing into the bulk begin at the pit.

The finally saturated value of the loading

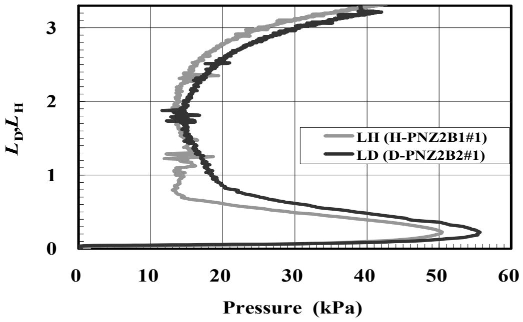

Fig. 4. Relation between the loading ratio and the pressure for the PNZ2B sample

ratio, D(H)/[Pd·Ni], is extraordinarily large; 3.3 both for D and H absorption. The specific heat release, $E_1 \approx 2.0$ (1.8) eV/atom-[Pd·Ni], in the first phase of the as-received PNZ2B1 and PNZ2B2 runs is also very large. These values of E_1 are divided by the final values of the loading ratio to give tentative value of the hydridation energy, $Q_{D(H)} \approx 0.55$ (0.50) eV/atom-D(H). This is tentative because the energy of oxygen pickup is not subtracted from E_1, since the oxidization fraction x is not known.

After finishing the #1 run, we evacuated the reaction chamber and made absorption runs without baking beforehand, which we call the #1A, and #1B runs. The final loading ratio was about 0.3 with the first-phase duration of about 120 minutes both in the #1A and the #1B. The first-phase energy E_1 as well as the above value of the loading ratio is smaller than those in the #1 run. However, the tentative values of $Q_{D(H)}$ are of the same order of magnitude as those in the #1 run.

After finishing the #1B run, we made forced deoxidization at 573 K. Figure 5 shows the #2 absorption runs using these samples. The first-phase duration is about 500 minutes, with peaks of power being 0.2 W for the H-run and 0.3 W for the D-run. In contrast to the #1 run, the pressure does not show the peculiar change. The values of D(H)/[Pd·Ni], E_1 and $Q_{D(H)}$ exceeded 2.0 (2.0), 1.5 eV/atom-[Pd·Ni] and 0.5 eV/atom-D(H), respectively, which are astonishingly large compared with those using the de-oxidized PZ samples [4,6].

The forced oxidization of the samples was performed by keeping them in the O_2 atmosphere at a temperature of 470 K or 570 K for 30 hours. The degree of oxidization, x, is calculated from the pressure difference between the beginning (0.3 MPa) and the end of the exposure to O_2 in the closed system. The values of x ranged from 0.000767 to 0.000732 in 470 K operation, and from 0.000921 to 0.000917 in 570 K operation.

Figure 6 shows the traces in the #3 absorption runs using the oxidized samples. We first notice that the peculiar pressure change observed in the #1 run has appeared again in the early stage of the first phase lasting for 500 minutes. The oxidized samples has almost recovered the large values of E_1, D(H)/[Pd·Ni] and $Q_{D(H)}$ of the as-received samples. There is recognized a trace of endothermic variation of the output power at the beginning of the deuterium run. However, the reproducibility of this variation should be examined.

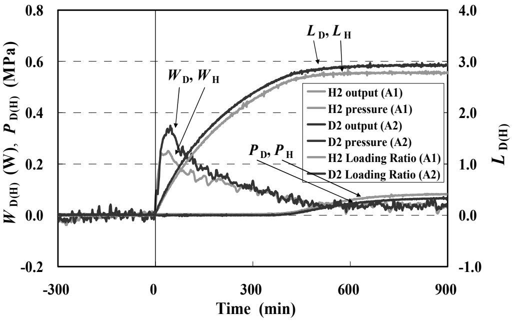

Fig. 5. The run after forced deoxidization

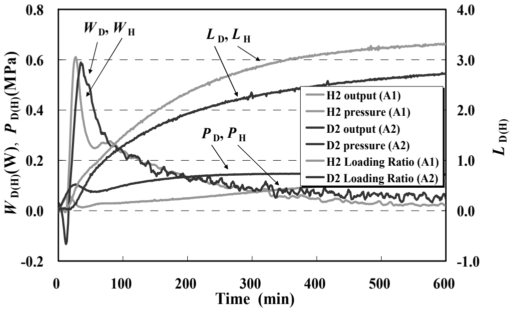

Fig. 6. The absorption run after forced oxidation (H-PNZ2B3#3 and D-PNZ2B4#3)

We reused the PNZ2B samples; the mixture of the PNZ2B1 and the PNZ2B3 samples is the PNZ2B5, while the PNZ2B2 and PNZ2B4 sample mixture is the PNZ2B6. Figure 7 shows the #1 absorption run of the reuse samples. The absorption parameters are D(H)/[Pd·Ni] ≈ 2.0 (2.0), $E_1 \approx 1.7$ (1.3) eV/atom-[Pd·Ni], and $Q_{D(H)} \approx 0.60$ (0.50)eV/atom-D(H). The #2 and #3 runs of the reused samples also showed that D(H)/[Pd·Ni], E_1 and $Q_{D(H)}$ are of the same order of magnitude as those in the #1 run.

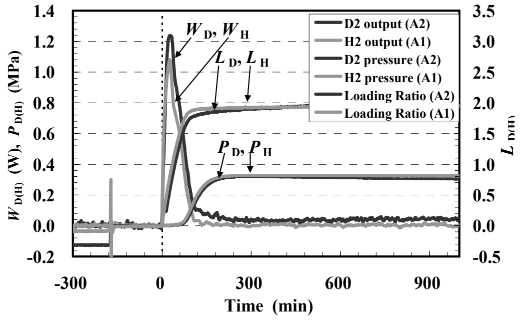

Fig. 7. Runs for the reused sample (H-PNZ2B5#1 and D-PNZ2B6#1).

Figures 8, 9 and 10 show the parameters E_1, D(H)/[Pd·Ni] and $Q_{D(H)}$ as histograms. The first-phase specific energy E_1 for deuterium is larger than that for hydrogen. The hydridation energy Q_D for deuterium is also greater than that for hydrogen. The ratio Q_D/Q_H is almost constant in the runs using PNZ2B1 through PNZ2B4, and the averaged value is about 1.22 ± 0.13, which appears to be a little larger than that expected for a chemical isotope effect.

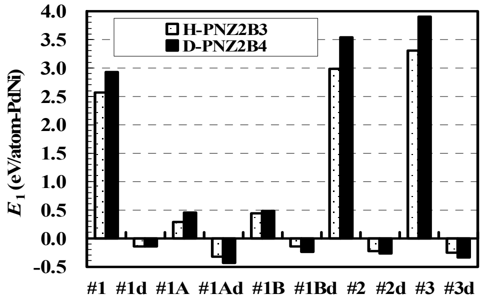

Fig. 8. E_1 for the samples H-PNZ2B3 and D-PNZ2B4.

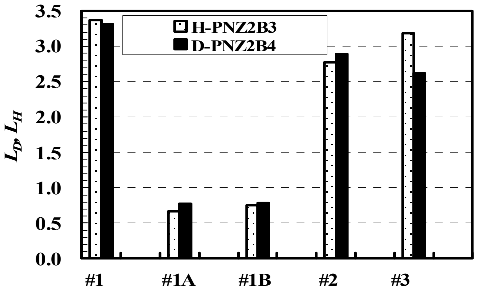

Fig. 9. D(H)/[Pd·Ni] for the samples H-PNZ2B3 and D-PNZ2B4.

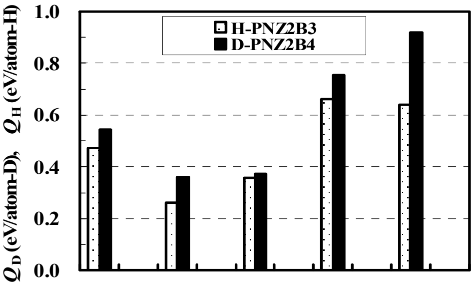

Fig. 10. Hydrydation energy, $Q_{D(H)}$, for the samples PNZ2B3, and PNZ2B4.

Next, we discuss time resolved parameters. The time-resolved specific sorption energy, or differential heat of hydrogen uptake, $\eta_{D(H)}$, defined as the output energy per one hydrogen isotope atom absorbed/adsorbed [4,6], are shown in Fig. 11 together with the heat evolution in the PNZ2B3#1 and PNZ2B4#1 runs. We notice that η_D (η_H) is relatively constant in contrast to the PZ samples whose first phase is divided into 1a and 1b phases [4,6]. The averaged value is 0.53 (0.47) for the first phase of these runs, which is averaged again over all runs to give $\overline{\eta}_{D(H)} = 0.60$ (0.53). In every cases of #1, #2 and #3 runs, the averaged value of η_D is larger than that of η_H, and these values are rather modest compared with those for the PZ samples.

Figure 12 shows the ratio of η_D to η_H. The value of η_D/η_H in the early stage of the first phase is about 1.5, and is significantly larger than the ratio $\overline{\eta}_{\mathrm{D}}/\overline{\eta}_{\mathrm{H}} = 1.12 \pm 0.16$ using the averaged values mentioned above. This is one of the reason why $Q_{\mathrm{D}}/Q_{\mathrm{H}}$ is a little larger than $\overline{\eta}_{\mathrm{D}}/\overline{\eta}_{\mathrm{H}}$, since the early stage heat evolution has larger weight in calculating the former. This might indicate that some nuclear effects including nuclear reactions could contribute to the heat evolution in the early stage of PNZ2B4#1 run.

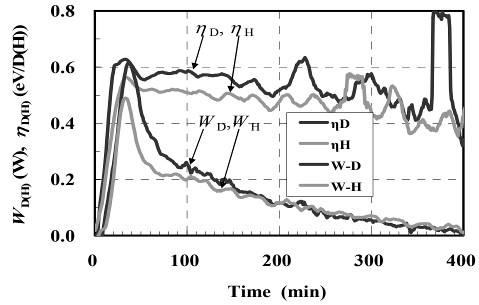

Fig. 11. Evolution of heat, W, and the time-dependent absorption energy, η, for D_2 gas and H_2 gas(H-PNZ2B3#1 and D-PNZ2B4#1).

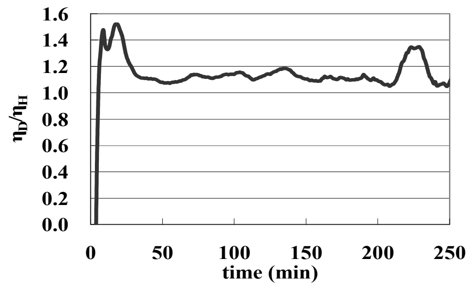

Fig. 12. Comparison of η_{D} with η_{H}.

5. conclusion

The PNZ2B sample, the Pd(0.04)Ni(0.29)Zr(0.67) oxide composite, has unique properties, and the results of the absorption experiments are summarized as follows;

(1) Observed loading ratio, D(H)/[Pd·Ni] ≈ 3.0, and specific heat release, $E_1 \approx 2.0$ eV/atom-[Pd·Ni], in the first phase of the absorption runs using as-received PNZ2B samples are both very large.

(2) It is deduced that Ni as well as Pd contributes to the first phase heat by hydrogen isotope absorption / adsorption at room temperature. It is inferred that the Pd atoms act as a catalyst for the hydrogen isotope absorption / adsorption of Ni.

(3) The hydridation energy $Q_{\mathrm{D(H)}} \approx 0.60(0.49)$ eV/atom-D(H) is about twice as large as that for the bulk Pd [7], and $Q_{\mathrm{D}}/Q_{\mathrm{H}}$ is about 1.22± 0.13, which appears to be suggesting the existence of heat component of nuclear origin.

(4) For samples after forced oxidization the loading ratio and the heat release were as large as those for the as-received samples. This result is similar to those for the #1 and #3 runs of the PZ samples [4,6].

(5) The PNZ2B samples, however, showed that heat release of the #2 run after the forced deoxidization is as large as that of the #1 run.

(6) The PNZ2B samples show anomalous change of gas pressure in the beginning of the first phase.

(7) There is no sub-phase transition, 1a / 1b. The time dependent sorption energy, $\eta_{\mathrm{D(H)}}$, is rather constant, and averaging over the first phase gives 0.60 (0.53) eV/atom-D(H).

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