

Hydrogen/Deuterium Absorption Property of Pd Fine Particle Systems and Heat Evolution Associated with Hydrogen/Deuterium Loading

T. Hioki¹, H. Azuma¹, T. Nishi¹, A. Itoh¹, J. Gao¹, S.Hibi¹, T.Motohiro¹, and J. Kasagi²

¹Frontier Research Center, Toyota Central R & D Laboratories, Inc., Nagakute, Aichi, Japan

²Research Center for Electron Photon Science, Tohoku University, Mikamine, Sendai, Japan

E-mail: hioki@mosk.tytlabs.co.jp

Abstract. Hydrogen absorption capacity and heat evolution upon loading with hydrogen/deuterium gas were measured for Pd-ZrO₂ nanocomposite obtained from Santoku Corporation. In order to examine the influence of oxidized Pd on both hydrogen absorption capacity and heat evolution, the measurements were performed three times repeatedly. Prior to each measurement, the samples were heat treated in vacuum at 523K for more than 2 hours. The first time measurement gave an apparent H/Pd ratio of 2.6 and a heat evolution of 2.6eV/Pd. During the first time measurement, the oxidized Pd was reduced to metallic Pd. It was found that the H/Pd ratio at 1MPa was slightly smaller than that of Pd bulk. It was also noted that Pd nanoparticles grow significantly during the cycles of absorption and desorption of hydrogen. When the sample was loaded with deuterium, intermittent heat evolutions as small as at most 0.1W were observed in the second stage where heat evolutions arising from chemical reactions were hardly expected.

1. Introduction

A very simple solid nuclear fusion reactor has recently been proposed by Arata and Zhang [1]. They have used a material of nano-sized (~5nm) Pd particles dispersed in ZrO₂ matrix. By simply pressurizing the material with deuterium gas, they have observed a long lasting difference in the temperature between the center of the sample powder and the outside surface of the sample vessel. When the sample was loaded with hydrogen gas, no such temperature difference was observed. Furthermore, by using a quadrupole mass spectrometer, they have observed a significant increase of ⁴He for the gas sampled from the powder pressurized with deuterium gas. From these facts, they have claimed a heat evolution arising from a deuteron-deuteron nuclear fusion reaction yielding ⁴He as ash.

Kitamura et al. [2] have constructed a flow calorimeter and measured quantitatively the heat evolution associated with loading of hydrogen or deuterium gas for Pd-ZrO₂ nanocomposite with Pd particle size of ~10nm. The material was obtained from Santoku Corporation and was different from those used by Arata and Zhang. Kitamura et al. have clearly observed a difference in the heat evolution between the loadings with deuterium and hydrogen in the second phase where heat evolution due to chemical reactions is not expected [2]. What seems to be important in the Arata and Zhang's experiment is that they have attained a very high value of hydrogen absorption capacity per Pd atom, i.e. D/Pd or H/Pd ratio, by using nano-sized Pd material. It has been known that attaining a D/Pd ratio larger than 0.88 is favorable to observe an excess heat in the electrochemical loading of Pd with deuterium [3]. Actually, a high value of hydrogen absorption capacity has been reported for nanoscale Pd particles embedded in ZrO₂ matrix prepared from Zr-Pd amorphous alloys [4]. Kitamura et al. [2] also reported a D/Pd or H/Pd ratio of 1.1 for the Santoku's Pd-ZrO₂ composite material, which far exceeds the reported value [5] of 0.74 for Pd bulk.

We have started to investigate the relationships between Pd particle size, hydrogen/deuterium absorption capacity and heat evolution upon loading with hydrogen/deuterium gas for nanoPd materials.

The results for Pd nanopowder and Pd- γ Al₂O₃ composite have been reported elsewhere [6]. In this paper, a similar study has been extended to Pd-ZrO₂ composite obtained from Santoku Corporation.

2. Experimental

2.1 Materials

The material used in this study was a composite of nanoPd and ZrO₂ (Pd-ZrO₂) synthesized by Santoku Corporation. The X ray diffraction pattern for the as-received sample showed that it consisted from PdO and ZrO₂. The contained amount of PdO was 35.4wt%. The crystal phases of the ZrO₂ component were monoclinic and tetragonal. The contained amount of each phase was roughly equal. The specific area was 38m²/g. As a reference for Pd bulk, Pd foils (99.95%, The Nilaco Corporation) with dimensions of 8mm × 30mm × 0.025mm were used.

2.2 Hydrogen storage capacity

A pressure-composition (PC) isotherm apparatus (Suzuki Shokan Co. Ltd) was used to measure hydrogen absorption capacity as a function of pressure up to about 1MPa at room temperature (300K). The purity of hydrogen and deuterium was 99.99999% and 99.995%, respectively.

2.3 Calorimetry

The heat evolution associated with loading of hydrogen isotope gas was measured with a flow calorimeter. The difference in the temperature between the inlet and outlet of the cooling water was measured with thermocouples of alumel-chromel. The flow rate of water was measured by using a Coriolis-force type flow meter. The temperature difference and the flow rate of water were registered every 30 seconds and used to calculate the heat power. An electric heater was mounted at the center of the sample vessel and used to determine the recovery rate of heat, i.e. the ratio of the calculated heat power with the measured temperature difference and the flow rate of water to the heat power supplied by the electric heater. A value of 0.55 was used as the recovery rate, which was almost independent on the species of the used gas (H₂, D₂, He), the gas pressure in the range 0 ~1 MPa, and the electric heater power in the range of 1~5W. In order to suppress the fluctuation and the drift of the measured output power, the calorimeter system was thermally insulated from the ambient atmosphere by using a thermal insulation material. The accuracy of the calorimeter was \pm 50mW. The gases were supplied into the sample vessel through a needle valve and a mass flow controller. The flow rate of gas was about 20ml/min.

3. Results and discussion

3.1 Hydrogen absorption capacity

The as-received Pd-ZrO₂ composite sample of about 10g was mounted in the sample vessel of the PC isotherm apparatus. First, in order to remove absorbed gases or molecules, the sample was evacuated for a day, heated up to 523K in vacuum and maintained at the temperature for about 2 hours, followed by natural cooling to room temperature. After these pre-treatments, hydrogen gas was supplied to the sample until the pressure of the sample vessel reaches a given value. At around the given pressure, about 30minutes were needed to achieve an equilibrium pressure. Thus, the hydrogen pressure was increased step by step up to 1MPa. After the course of this first time measurement, the sample was again evacuated for a day, heated up to 523K and maintained at the temperature for about 2 hours, followed by natural cooling to room temperature. Then, the second time measurement was performed following the same procedure as those of the first time.

In Fig.1, the relationship between pressure and composition (H/Pd) are shown for three times successive measurements. It is seen that in the first time measurement, H/Pd ratio at 1MPa reaches a value of 2.6, while this value decreases greatly to a value of 0.70 in the second and third measurements. This difference is attributed to the fact that the Pd particles are initially oxidized and reduce to metallic Pd during the first time measurement. Then, in the first time measurement both of the following chemical reactions occur :



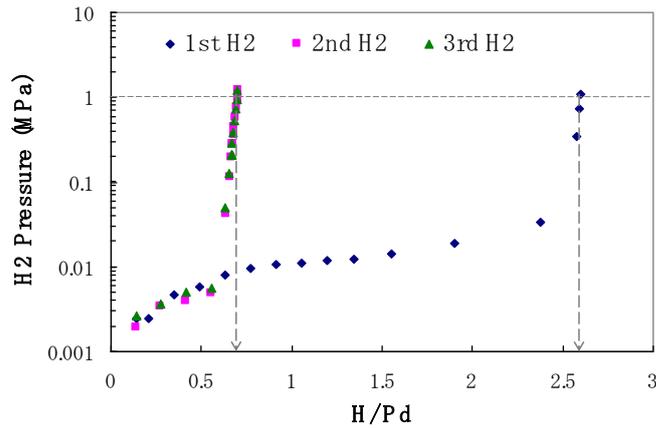


Fig.1 - Pressure- composition isotherms for Pd-ZrO₂ composite. The results of three times repeated measurements are shown.



The water formation reaction (1) gives an apparent H/Pd ratio of 2.0, and the hydride formation reaction (2) gives a true value of hydrogen absorption capacity x . The value of x is obtained from the experiment in the second or the third time measurement and x is 0.70 as seen in Fig.1. Therefore, when the Pd particles are nearly 100% oxidized, an apparent H/Pd ratio of ~2.7 is obtained. The observed value of 2.6 indicates that 95% of Pd in the as- received sample is in the chemical state of PdO.

The PC isotherms were also measured for Pd foil samples of about 3g. The measurements were repeated two times. For this sample, no difference in the H/Pd ratio at 1MPa was seen between the two measurements, indicating that the foil sample was nearly 100% metallic. The H/Pd ratio for this sample was 0.74. This value agrees with the literature value [5] for Pd bulk. Therefore, the H/Pd value of 0.70 for the Pd-ZrO₂ composite sample is slightly smaller than the value of Pd bulk. This is contrary to the expectation that the hydrogen absorption capacity for nano-sized Pd particles is increased compared to that for Pd bulk. Similar results have been observed for Pd nanopowder and Pd- γ Al₂O₃ composite, as reported elsewhere [6].

3. 2 STEM observation

In order to examine the size and distribution of the Pd particles, scanning transmission electron microscope (STEM) observations with an electron beam focused to less than 1nm were performed for the samples as-received and after the three times PC isotherm measurements. From Fig.2 (a), it is seen that the size of the Pd particles (white spot) for the as-received state is roughly about 10nm. Fig.2 (b) and (c) show the lateral distribution of characteristic Zr(L) and Pd(L) X-ray intensity, respectively. It is seen from Fig.2 (b), (c) or from Fig.3 (b), (c) that the Pd particles do not distribute uniformly in the ZrO₂ matrix. From Fig.3(a), it is seen that the size of the Pd particles after the PC measurement is 15-20nm, which is significantly larger the initial value. This fact indicates that Pd particles grow during the hydrogen absorption and desorption cycles. Similar growth of Pd nanoparticles during the cycles of absorption and desorption of hydrogen has also been reported for nanoPd powder and Pd- γ Al₂O₃ composite [6]. It should be mentioned that the measured H/Pd ratio, i.e. 0.70, is for Pd particles with a size significantly larger than the initial value determined for the as-synthesized sample.

3.3 Heat evolution upon loading with hydrogen isotope gases

The as-received Pd-ZrO₂ composite sample of 51.4g (Pd :15.6g) was mounted in the sample vessel of the calorimeter. The sample was first evacuated for two days and heated up to 523K in vacuum and maintained at the temperature for about 2 hours, followed by natural cooling to room temperature. Then, deuterium gas was supplied to the sample at a flow rate of 20ml/min with a mass flow controller up to 0.4MPa. From 0.4MPa to 1.0MPa, the flow rate was controlled manually with a needle valve, and the

flow rate was in the range 20–40ml/min. When the pressure reached the value of 1MPa the gas supply was stopped and the sample was maintained under the fixed pressure of 1MPa. Here, we define the first stage as the period where the pressure was raised from 0 to 1 MPa, the second stage as the period where the sample was maintained under the constant pressure of 1MPa. As in the case of hydrogen absorption capacity measurements, the measurement of heat generation upon loading of deuterium /hydrogen gas was repeated three times. Prior to each measurement, the sample was heat treated in the same way as the first time measurement. In Fig.4 (a), (b) and (c), the heat power as a function of time is shown for the first time loading with D₂, the second time loading with D₂ and the third time loading with H₂, respectively. The variation of pressure with time is also shown in Fig.4. It is clearly seen that the heat evolution in the first stage is remarkable in the first time measurement while it decreases greatly in the second or third time measurement. This behavior is quite similar to that of hydrogen absorption capacity, suggesting that the heat evolution in the first stage is related with the chemical reactions (1) and (2). In fig.5, the variation of the heat evolution in the first stage with the order of measurement cycle is shown. The experimental values are compared to the estimated ones. The estimation was made assuming that in the first time measurement, both of the reactions (1) and (2) contribute to the heat evolution while only the reaction (2) in the second and third time measurements. The values of $\Delta H(\text{water})=-178\text{kJ/molPd}$ [7] and $\Delta H(\text{hydride})=-40\text{kJ/molH}_2$ [8] were used. It was further assumed that $\Delta H(\text{hydride}) = \Delta H(\text{deuteride})$ and the ratio of the oxidized Pd to the total Pd before the first time measurement was 95%. It is seen in Fig.5 that the heat generated in the first stage is largely explained by the chemical reactions (1) and (2). Therefore, in the first stage it is difficult to identify the heat evolution from nuclear origin, if any. However, in the second stage, any chemical reactions are hardly expected to occur. In Fig.6, the same figure as Fig.5 is shown with the vertical axis magnified by ten times. It is noted that in the second stage a small heat evolution is observed intermittently for the first and second time loadings with D₂ while no such heat evolution is observed in the third loading with H₂. Similar behavior of heat evolution in the second stage has also been reported for nanoPd power and Pd- γ Al₂O₃ composite [6]. The heat evolution of the second stage observed in the present study seems to be considerably smaller compared to that reported by Kitamura et al. [2]. It is required to enhance the heat power in the second stage in order to clarify the origin of the observed anomalous heat evolution.

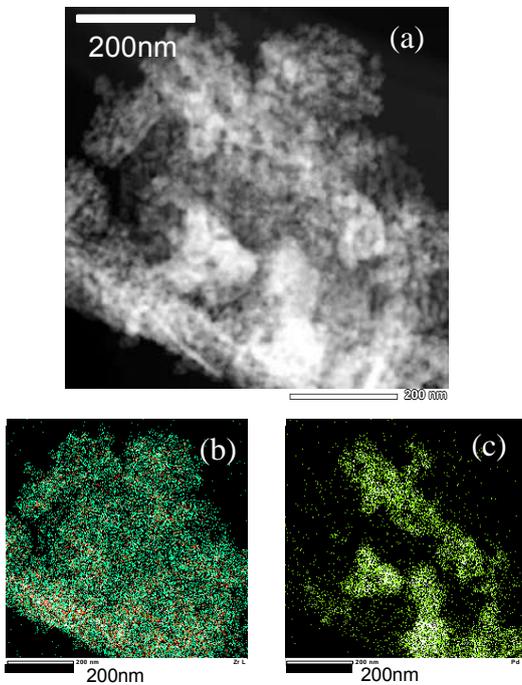


Fig.2 - (a)STEM image of the as-received sample, (b) Zr(L) image, (c) Pd(L)image

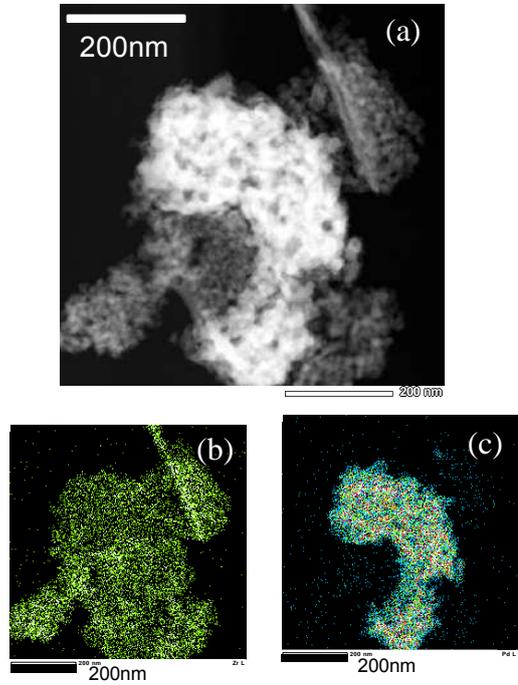


Fig.3 - (a)STEM image after measurements of H/Pd, (b) Zr(L) image, (c) Pd(L) image

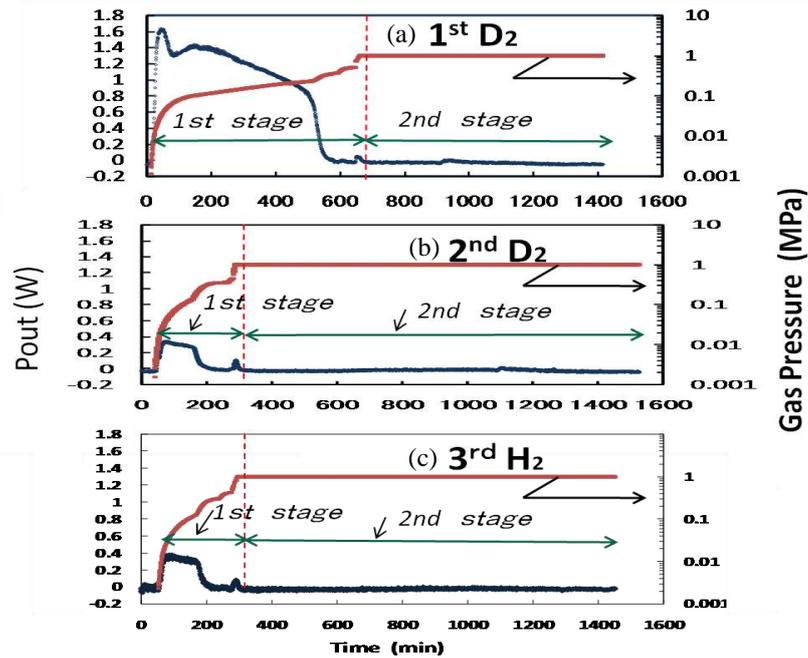


Fig.4 - Heat power and gas pressure as a function of time for Pd-ZrO₂; (a) the first cycle loading with D₂, (b) the second cycle loading with D₂, (c) the third cycle loading with H₂.

4. Summary

Hydrogen absorption capacity and heat evolution with loading of hydrogen isotope gases were measured for composite samples of Pd-ZrO₂ obtained from Sankoku Corporation. The followings were found.

- (1) The chemical state of Pd in the as received powder was 95% PdO. As a result, the first time loading with hydrogen gave an apparent hydrogen absorption capacity at 1MPa as large as H/Pd = 2.6 and heat evolution in the first stage as large as 2.6eV/Pd. These values are largely understood by taking into account the two chemical reactions; the water formation reaction and the hydride formation reaction. The PdO was reduced to metallic Pd during the first time measurement.
- (2) In the second or third time measurement of hydrogen absorption capacity, a true value of H/Pd = 0.70 was obtained. This value is slightly smaller than the value of Pd bulk.

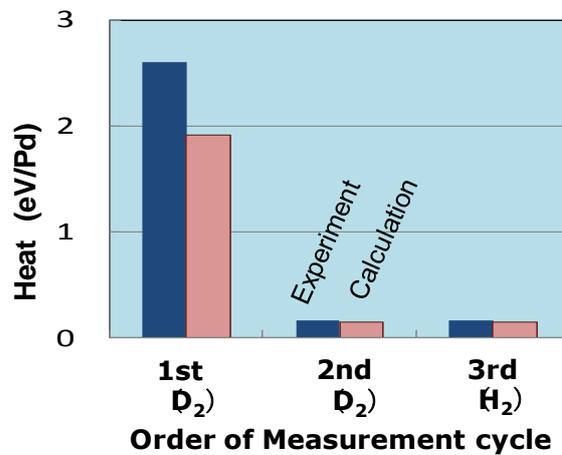


Fig.5 - The variation of the heat generated in the first stage with the order of measurement cycle. The experimental values are compared to the calculated ones.

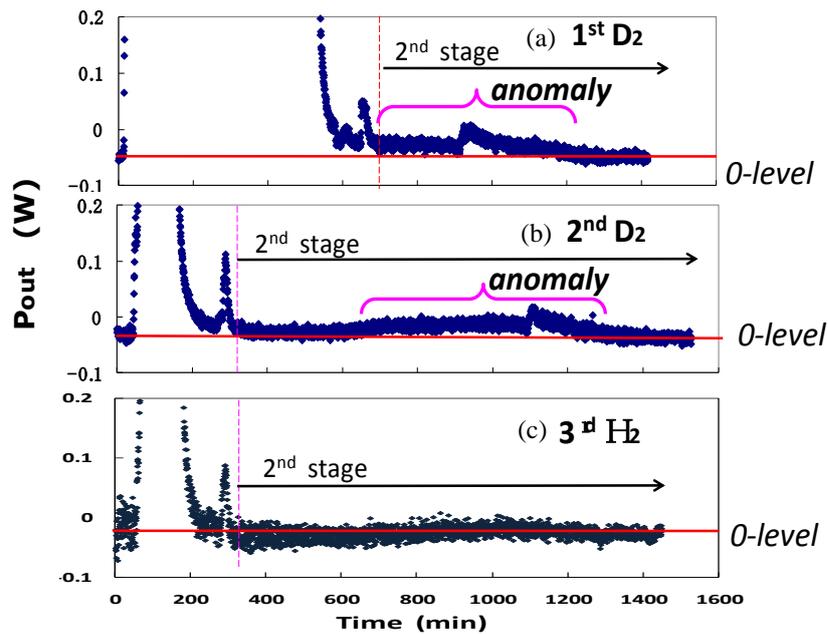


Fig.6 - Heat evolution in the second stage. The vertical axis of Fig.3 is magnified by ~ 10 times.
 (a) the first cycle loading with D₂, (b) the second cycle loading with D₂, (c) the third cycle loading with H₂.

(3) The size of the Pd particles was found to be increased significantly during the repeated measurements of hydrogen absorption capacity.

(4) When the sample was loaded with D₂ gas, a very small heat power was observed intermittently in the second stage where chemical reactions are hardly expected to occur.

Acknowledgement

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