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Edited by Masahiro Kishida

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#### PREFACE

This is the proceedings of the 20th Meeting of Japan CF-Research Society (JCF20), which was held on December 13-14, 2019 at Reference Hakata Eki-Higashi Rental Room, Fukuoka, Japan. In this meeting, 15 presentations were given and 9 papers were submitted to the editorial board. They have been peer reviewed by the referees, and revised for the publication as the proceedings.

For all meetings, JCF1 through JCF19, we published the Proceedings. For the meetings after JCF4, we published electronic versions of the proceedings on our web-site http://jcfrs.org/proc\_jcf.html in addition to their printed versions. In view of low efficiency and low effectiveness in distributing information, we decided to discontinue the printed version for the meetings, JCF12. Only the electronic versions have been published thereafter. Any questions and comments are welcome for the proceedings.

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Finally, we would like to thank all the participants and the people who have collaborated in organizing this meeting.

Editor-in-Chief Masahiro Kishida, Kyushu University October 2020

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## Development of reaction system with small chamber for fundamental experiments measuring anomalous heat effect

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Abstract It is known that anomalous heat is generated when hydrogen or deuterium is absorbed by nickel or palladium. Recently, we developed a small reaction chamber system and conducted fundamental experiment to validate the anomalous heat. The chamber system has a constant volume of about 2mL for reaction, which is made from SUS316 and SUS316L. Sample (PNZ10r, provided by Technova Inc.) and hydrogen gas are put inside of the reaction chamber. The sample temperature is measured by K-type thermo couple, after initial temperature in the chamber system is set to be 60 °C. To confirm the temperature increase for mixture of hydrogen and PNZ10r, mixture of nitrogen and PNZ10r is also tested. When the hydrogen gas is absorbed by PNZ10r, temperature rise of about 3K is observed. This temperature increase is larger than that of control experiment using nitrogen. Thus, it can be considered that the anomalous heat generation is occurred.

Keywords: Anomalous heat effect, Hydrogen gas, Small reaction chamber

## 1. Introduction

It is known that anomalous heat is generated when hydrogen or deuterium is absorbed by nickel or palladium [1-4]. The anomalous heat is observed in several patterns: H<sub>2</sub> or D<sub>2</sub> gas absorbing of nano-sized metal composites [1-2], D<sub>2</sub> gas absorbing of Pd powder [3], and electrolysis using Ni film [4]. Especially, the way that metal powder absorb gas is notable. Large anomalous heat is relatively observed in the combination nickel-based powder and hydrogen gas, or palladium-based powder and deuterium gas [2-3].

We want to develop a new energy generator using the anomalous heat, which is based on very high compression obtained by collision around reaction chamber center of the high-speed multi-jets entering repeatedly from outside of reaction chamber. [5-8] This is because some computations of the collision of multi-jets around chamber center indicate both of high pressures over 50 MPa and high temperature over 2000 K, while combustion experiments using the multi-jets colliding show potential of high power and high thermal efficiency. [9-10]

Toward the next step, we also made a small closed reaction system having a constant volume, in order to check safely the anomalous heat effect in detail while varying the operating conditions in a relatively short period with low cost.

## 2. Experimental device

Figure 1 shows outline of the reaction system. The reaction system is constructed of reaction chamber, small test tube, K-type thermocouple, two pressure gauges, three valves, gas supply device, scroll pump and bead bath. This reaction system is designed with sufficient endurance margin at condition of 100 °C and 1 MPa, to keep safe in case of huge heat is generated in experiments.

The sample is put in small test tube inside of reaction chamber. In this report, a small amount of PNZ10r (Pd1Ni10/zirconia powder, about 100 nm particle size, 1.0 g provided by Technova Inc.) [11] is employed as the sample. Sample temperature is measured by sheathed K-type thermocouple (HTK0227, made by Hakko electric co., ltd.) whose tip is embedded in the sample. Pressure of the gas provided into the chamber is measured by two pressure gauges (CG-1.6MPA-60, made by YAMAMOTO KEIKI MFG. Co., LTD.). To prevent breaking down the reaction system, safety valve opens when pressure in the reaction chamber exceed 1 MPa. For the purpose of promoting the heat generation, the reaction chamber and sample are preheated to 60 °C by bead bath (MD-MINI, made by Major Science) before experiment. Aluminum beads is used for the bead bath. Gas is supplied from gas supply device (LMX2-J-A7, made by FRONTO Co., Ltd). Scroll pump (ISP-250C, made by ANEST IWATA Corporation) is used for evacuation.

Specification of the reaction system is shown in Table 1. About 2 mL reaction chamber is made from SUS316 and SUS316L. Test tube put in the reaction chamber is made from glass. Ultimate pressure of scroll pump is 1.6 Pa. Maximum pressure allowable for the gas supply device, i.e., withstanding pressure, is 0.7 MPa, while maximum temperature that can be set of the bead bath is 100 °C.



Fig. 1 Outline of the reaction system

<b>Table 1</b> Specification of the reaction syste	m
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Material of reaction chamber	SUS316L
Volume of reaction chamber	2 mL
Material of test tube	glass
Ultimate pressure of scroll pump	1.6 Pa
Maximum pressure of loading gas	0.7 MPa
Maximum temperature of bead bath	100 °C

## 3. Procedure of experiment

Procedure of experiment is shown in Fig. 2. First, the sample (PNZ10r) is set in the test tube and put in the reaction chamber. Then, the reaction chamber is evacuated by using scroll pump. After that, preheating with the bead bath is started. When the sample temperature increases to a certain target value, the preheating is stopped. As the final step before reaction, H<sub>2</sub> or N<sub>2</sub> gas loaded into the chamber from gas supply device and we measure temperature increase with K-type thermocouple. At the end of the reaction experiment, the loaded gas is exhausted. The chamber is evacuated again not to leave the gas in it.



Fig. 2 Procedure of experiment

## 4. Experimental results

Experimental conditions are shown in Table 2. Same sample of PNZ10r is used in the experiments. Because of low reactivity of nitrogen with a metal, N<sub>2</sub> gas is used for control experiment. Experiment No. 1 with the nitrogen gas is conducted as control experiment for No. 2 with the hydrogen gas. Results of each experiment are shown in Fig. 3 and Fig. 4. Two labels "Start" and "End" are show the time of beginning of gas loading and the time of gas exhausting, respectively.

Figure 3 shows the result of experiment No. 1 with the nitrogen gas. In this experiment, temperature increase of PNZ10r is 2.2 K. Sample temperature after preheating by 60 °C bead bath is 45.2 °C. When N<sub>2</sub> gas is loaded in reaction chamber, the sample temperature start increasing from 45.2 °C. The sample temperature reaches the maximum temperature 47.4 °C about 3 minutes later from the start of the experiment. After that, the sample temperature stays around 47.1 °C until the end of the experiment about 30 minutes after. Because of low reactivity of nitrogen with a metal, it is considered that the temperature increase of experiment No. 1 (47.4 °C about 3 minutes later from the start 3 minutes later from the start) is caused by compression of N<sub>2</sub> gas in the reaction chamber. In the same way, it is considered that the temperature decline after the gas exhausting is caused by expansion of the N<sub>2</sub> gas in the reaction chamber. Since the loading gas is room temperature, it is considered that the sample temperature temperature temporarily dropped after start of the gas loading.

Figure 4 shows the result of experiment No. 2 with the hydrogen gas. In this experiment, temperature increase of PNZ10r is 3.2 K in this experiment. Sample temperature after preheating by 60 °C bead bath is 45.5 °C. When H<sub>2</sub> gas is loaded in reaction chamber, the sample temperature start increasing from 45.5 °C. The sample temperature reaches the maximum temperature 48.7 °C about 2 minutes later from the start of the experiment. After that, the sample temperature stays around 48.5 °C until the end of the experiment about 30 minutes after. Then, in the experiment No. 2, the sample temperature increases

faster than that of No. 1 and keeps higher than the preheated temperature even after the gas exhausting. These differences suggest the temperature rise caused by other than gas compression.

Table 2Experimental conditions					
Experiment number	No. 1	No. 2			
Kind of gas	Nitrogen	Hydrogen			
Gas pressure	0.3 MPa	0.3 MPa			
Temperature of bead bath	60 °C	60 °C			
(Limit of temperature = $100 \text{ °C}$ )	00 C				
Sample name	PNZ10r	PNZ10r			
Sample mass	1.0 g	1.0 g			







Fig. 4 Result of experiment No. 2

## 5. Comparison of results in the experiments

Figure 7 shows the comparison of results in experiment No. 1 and No. 2. Summary of the results in the experiments is shown in Table 3. The start time of each experiment is adjusted to 0.

According Fig. 7, the maximum sample temperature during the experiment No. 2 with the hydrogen gas is larger than that of experiment No. 1 by 1.3 K. Temperature increase for experiment No.2 (Hydrogen) larger than that for experiment No.1 (Nitrogen), i.e., maximum temperature difference of about 1.0 degree between No.2 and No.1 is observed again in the other day. In addition, according to Table 3, the temperature increase of PNZ10r in the experiment No. 2 is larger than that of experiment No. 1 by 1.0 K. This result may show that heat generation occurred in hydrogen absorption of PNZ10r. Accuracy of temperature measured will be with increment of about 0.1 K, which is minimum scale value. Then, the temperature rise continues over 30 minutes. It may be considered that not only adsorption heat, but anomalous heat is generated in the experiment No. 2, although we need to conduct more experiments at higher temperature conditions for longer time in order to distinguish both these heat generation.



Fig. 7 Comparison of results in experiment No. 1 and No. 2

Experiment number	No. 1	No. 2
Initial temperature	45.2 °С	45.5 °C
Maximum temperature	47.4 °C	48.7 °C
Temperature increase	2.2 K	3.2 K

 Table 3 Summary of results in the experiments

## 6. Conclusion

We developed a reaction system with small chamber and conducted fundamental experiment. In the fundamental experiment using 0.3 MPa H<sub>2</sub> gas and 1.0 g of PNZ10r, and 60  $^{\circ}$ C bead bath, 3.2 K of sample temperature increase is obtained.

In the experiments using  $H_2$  gas, larger temperature increase is obtained, compared to control experiments using  $N_2$  gas. Thus, heat generation occurring in  $H_2$  gas absorption of PNZ10r can be said to be observed. It is necessary to conduct more experiments at higher temperatures for longer time in order to distinguish the temperature increase caused by adsorption heat or anomalous heat. It is also necessary to record the time history of pressure in the reaction chamber in order to investigate pressure dependence of heat generation.

We will conduct more experiments by changing pressure of  $H_2$  gas, initial temperature, and kind of sample. In the near future, we will examine the relationship between the magnitude of temperature increase and pressure of  $H_2$  gas, initial temperature and kind of sample.

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## **Enhancement of Excess Thermal Power in Interaction of Nano-Metal and H(D)-Gas**

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*Abstract* Significant enhancement of excess thermal power by the anomalous heat effect (AHE) has been attained by our latest experiments on interaction of binary nanocomposite metal powders and H (or D) gas at elevated temperature of 300-400 °C. Observed excess thermal power levels in average were 10, 86 and 186 W/kg-sample for PNZ10, PNZ10r and PNZ10rr, respectively with deuterium-gas. In addition, levels in average were 11, 117 and 226 W/kg-sample for CNZ7, CNZ7r and CNZ7rr, respectively with light hydrogen gas. Generation of excess thermal power was very reproducible by week cycle runs of heating power on/off mode, and was steady for several days in each elevated temperature run.

Key words: anomalous heat, enhancement, Ni-based, nano-composite-metals, hydrogen gas, elevated temperature, 200 W/kg, excess thermal power, repeated recalcination, several weeks run

### I. INTRODUCTION

The anomalous heat effect (AHE) by the interaction of hydrogen-isotope-gas and nickel-based nano-composite samples as Pd-Ni/zirconia (PNZ) and Cu-Ni/zirconia (CNZ) powder samples at elevated temperatures around 300 °C has been studied intensively [1,2] under the NEDO-MHE project in 2015-2017 [3], for verifying the existing of the phenomenon and finding conditions of excess power generation in controllable way. As reviewed in ref. [4], the 8 year-long (2008-2015) series of study on AHE by interaction of metal nanoparticles and D(H)-gas under the collaboration of Technova Inc. and Kobe University has become the basis for the collaborative research of NEDO-MHE. The AHE phenomenon has been replicated by independent experiments at Tohoku University as well as at Kobe University under the collaboration study of the NEDO-MHE project [5, 6, 7]. Observed excess thermal power level of AHE were on the level of 3-20 W, and more enhancement was required for industrial application.

To scale up the AHE power level, study has been extended [8, 9] independently at Kobe University as the collaboration project with Technova Inc., after the 2015-2017 NEDO-MHE project. We have found that the re-calcination of used metal composite powder sample was very effective to enhance excess thermal power by the succeeding hydrogen charging runs at elevated temperature as reported in our ICCF22 presentation [10] and paper [11].

In this paper, we report that further significant enhancement of excess thermal power has been obtained by using the third re-calcined samples as PNZ10rr (Pd1Ni10/zirconia) and CNZ7rr (Cu1Ni7/zirconia). The gas-turbulence effect by large local AHE has been observed in all elevated temperature runs, in which we observed generation of over 50 W excess thermal powers with rather steady continuation for

weeks. We summarize results of AHE in comparison of excess thermal power data by the first calcined sample (PNZ10 or CNZ7), the second calcined sample (PNZ10r or CNZ7r) and the third calcined sample (PNZ10rr or CNZ7rr). We used deuterium gas for PNZ-type samples, while light hydrogen gas for CNZ-type samples. We have observed similar levels of excess thermal power for either deuterium or light-hydrogen gas, by some reasons in underlying mechanisms to be elucidated in future.

These observations must be circumstantial evidences of some nuclear reactions for underlying mechanisms of the AHE, as predicted by the condensed cluster fusion theory (CCF/TSC theory) by Akito Takahashi (see many papers downloadable at Research Gate [12]). For an introduction of CCF/TSC theories, the review papers [13, 14, 15] are recommendable.

The series of our study on AHE is a kind of spin-off subjective which has been developed after the about 20 years research of "cold fusion" started by the notorious F-P announcement in 1989[16]. A dream of potential clean portable nuclear energy, which would save the world global warming problem by CO2 accumulation, was a hope by the "cold fusion" (CF) phenomenon in 1990s, if really existing. However, the so called reproducibility problem has blocked the extension of researches by the original method of heavy water electrolysis with Pd cathode, although worldwide efforts by limited number of continuing researchers have gradually accumulated experimental results and theoretical aspects [17, 18, 19, 20, 21]. People have conceived that the difficulty of reproducibility arises by the material problem, although the CF occurrence might be on/near surface of Pd (or some other metals) from the consequences of many research works [20, 21]. Microscopic material condition at surface of metal electrode of electrolysis is too complex to control the optimum CF generating conditions. The hydrogen-gas (D or H gas) loading methods, especially the method using Pd nanopowder [22] was a kind of spin-off approach to realize reproducible results of AHE. The gas loading method has been greatly extended by the NEDO-MHE works [3], toward works using metal nano-composite samples with H(or D)-gas interactions at elevated temperatures [1-7] to report enhanced level of sustainable AHE. In Japan, the Tohoku University & Clean Planet collaboration, Nissan Motors group, Kyushu University, Iwate University, Technova & Kobe University collaboration and other groups are active now in the MHE (nano-Metal Hydrogen Energy) study based on the gas loading method [23, 24]. In the world, the INFN/Frascati group, Russian groups, French groups, USA groups are making active research efforts based on some kinds of gas-loading method. See related papers in recent JCMNS publications [21] in 2015-2020. The extending studies by the nano-metal composite samples and H(D)-gas interaction may look like passing through a breakthrough for the development of ecofriendly hard-radiation less energy sources. The results of present work may provide a step to that way.

#### II. EXPERIMENTAL METHODS AND PROCEDURE

The fabrication procedures of Pd-Ni/zirconia and Cu-Ni/zirconia for nanocomposite samples were described in our previous papers [1-9, 11]. The outline is 1) making thin (ca. 10 micron) amorphous metal ribbons of Pd<sub>x</sub>Ni<sub>y</sub>Zr<sub>z</sub> or Cu<sub>x</sub>Ni<sub>y</sub>Zr<sub>z</sub> metal composite alloys by the melt-spun method, 2) calcination in electric oven at ca. 450 °C for 120-180 hours, and 3) making ca. 0.1mm size powders by automatic mortaring machine. The atomic ratios of x/y/z are from 1/10/20 to 1/7/14, approximately. In the present work, we used Pd1/Ni10/Zr20 and Cu1/Ni7/Zr14 for PNZ10 and CNZ7 samples, respectively. After the first H(or D) gas charging and elevating temperature runs (#M-N, N=1,2,3), we took out the sample from RC (reaction chamber) to make recalcination in electric oven in ambient air with ca. 450 °C for ca. 180 hours. Then we reused for the second H(D)-charging and temperature-elevation runs (#M-N, N=1,2,3).

Between M=1 and 2 or M=2 and 3, we made so called baking treatment with 250-450 °C RC average temperature under vacuum-evacuation to meet the final RC pressure of less than 1 Pa. The second and third re-calcined samples are renamed with suffix r, as PNZ10r (or CNZ7r) and PNZ10rr (or CNZ7rr). The C system schematics for AHE calorimetry at Kobe University has been many times shown [1, 2, 4 -9, 11].

Calorimetry calibration data are given in [8] for TC1-TC6, TC2-TC6, and RTDav-TC6, by using blank sample of 1mm diameter zirconia beads (ca. 1.4 kg), for oil flow rate 18.4 ccm. For heating up RC, we used constant power supply units by Keithley Co., so that we did not need any correction for input heater power variation for [W1, W2]= [120, 80] W and [140, 95] W ET (elevated temperature) runs.

H (or D) gas was initially filled in Gas Cylinder having volume of 4 litters (for H-gas) and 2 litters (for D-gas), and fed to RC through Super Needle Valve. Initial pressure of Gas Cylinder was 0.4 to 1.0 MPa. By adjusting the SNV path size, we set gas flow rate as it took about 60 min to reach the equilibrium pressures at Ps and Pr [1-9], for the case of blank calorimetry runs. Here Ps is pressure of source gas cylinder, and Pr is pressure of RC. When we had the AHE of significant amount, evolution data of Pr and Ps were changed significantly from the blank runs. From the variation of Ps and Pr, we could calculate rate of H (or D) gas molars (or number of atoms) transferred by the runs. For present works, H-gas was used for CNZ7rr runs, and D-gas was used for PNZ10rr runs.

Typical patterns of the AHE experiments are as follows;

0) baking the sample (#1-0, #2-0),

1) H (or D) gas charging to RC at room temperature (RT) (heaters: [0, 0], #1-1, #2-1),

2) elevate RC temperature (heaters: [120, 80], #1-2, #2-2), run from Monday to Friday

3) cool RC to RT (heaters: [0, 0], #1-3, #2-3), from Friday to Monday

4) elevate RC temperature (heaters: [140, 95], #1-4, #2-4), from Monday to Friday Actual run-tables are given in Table-1 and 2, respectively for PNZ10rr and CNZ7rr.

		(	5	1 0	,
Run Number ID	W1, W2 (W)	Gas Fill Ps Pressure	Starting Time	RTD4 max (deg C)	Wex max (W) by RTDav
PNZ10rr #1-0	140, 40	Baking	2019/8/23		
PNZ10rr #1-1	0, 0	0.468 D2 MPa	2019/8/26	28.5	1
PNZ10rr #1-2	120, 80		2019/8/26	288.3	75.2
PNZ10rr #1-3	0, 0		2019/8/30		0
PNZ10rr #1-4	140, 95		2019/9/2	326.5	86.5
PNZ10rr #1-5	0, 0		2019/9/6	4	
PNZ10rr #1-6	140, 95		2019/9/18	327.4	87.1
PNZ10rr #1-7	0, 0		2019/9/20		
PNZ10rr #2-0	140, 40	Baking	2019/9/25		
PNZ10rr #2-1	0, 0	0.468 D2 MPa	2019/9/30	26.7	0.2
PNZ10rr #2-2	120, 80		2019/9/30	288.5	79.4
PNZ10rr #2-3	0, 0		2019/10/4		0
PNZ10rr #2-4	140, 95		2019/10/7	326.20	87
PNZ10rr #3-0	140, 40	Baking	2019/10/16		
PNZ10rr #3-1	0, 0		2019/10/21	26.8	0.2
PNZ10rr #3-2	120, 80		2019/10/21	288.6	77.5
PNZ10rr #3-3	0, 0		2019/10/25		
PNZ10rr #-3-4	140, 95		2019/10/28	326	86.5

## Table-1: Run table of PNZ10rr (438g PNZ10rr sample + 498g zirconia filler)

Table 2: Run Table of CNZ7rr (340g CNZ7rr sample + 1011g zirconia beads filler)

Run Number ID	W1, W2 (W)	Gas Fill Ps Pressure or	Starting Time	RTD4 max (deg C)	Wex max (W) by RTDav
CNZ7rr #1-0	140, 40	Baking under Evac.	2019/11/6		
CNZ7rr #1-1	0, 0	Ps=0.564 MPa	2019/11/11	27	0.3
CNZ7rr #1-2-1	120, 80		2019/11/11	284.6	73.1
CNZ7rr #1-2-0	<mark>0, 0</mark>		2019/11/11		
CNZ7rr #1-2-2	120, 80		2019/11/12	284.8	<mark>75.5</mark>
CNZ7rr #1-3	0, 0		2019/11/15		
CNZ7rr #1-4	140, 95		2019/11/18	324	83.2
CNZ7rr #2-0	140, 40	Baking under Evac.	2019/11/25		
CNZ7rr #2-1	0, 0	Ps=0.560 MPa	2019/11/27	31	. 3
CNZ7rr #2-2	120, 80		2019/11/27	285.6	72.6
CNZ7rr #2-3	0, 0		2019/11/28		
CNZ7rr #2-4	140, 95	Not done			

## **3.** RESULTS AND DISCUSSIONS

## 3.1 Heat Generation by PNZ10rr and D-Gas

We show a typical example of on-line data display (by NI Lab-View) in a rise-up phase of ET (elevated temperature) run of PNZ10rr #1-4, in Fig.1.



Fig.1: Typical rise-up time-evolution of RC (reaction chamber) temperatures (RTD1-4; upper left), oil outlet (TC1, TC2, TC3), inlet (TC6) and upper flange center (TC4) temperatures (lower left), pressures (upper right) and neutron rate (green; lower right), for PNZ10rr #1-4 [140, 95] run

We see start of anomalous excess temperatures rise of RTD1 and RTD2 (3 and 6 cm from bottom of RC (reaction chamber)), after temperatures exceeded ca. 300 °C (see upper left display), deviating upward from the indicial response (1.0 minus exponential saturating curve with calorimeter time constant) of calibration run with pure zirconia beads. An apparent neutron count increase (green in lower right display) looks correlating to the excess temperature rise of RTD1, 2, although neutron yield is close to natural background level. Very strangely, temperature at upper flange center by TC4 (outside of the hydrogen gas inlet/outlet tube) rises up steeply and suddenly becomes "flat" (see lower left display). We have reported already that gas-turbulence inside RC happens during strong local AHE [10, 11] which made underestimation of oil flow calorimetry by TC1, 2, 3 temperatures (as you see downward distortion; lower left display and see also Fig.2). As shown in Fig.2, strange evolution of TC4 temperature continues. Obviously, oil-outlet temperature monitors (TC1, 2 and 3) are distorted downward correspondingly, although temperatures (by RTD1, 2, 3, 4) in RC are increasing smoothly (upper left display).



Fig.2; Rise-up data display-2 for PNZ10rr #1-4 run



Fig.3 Rise-up data-3 for PNZ10rr #1-4 run

After that, RC temperatures have reached at some equilibrium state as seen in Fig.3. However, to our surprise, TC4 temperature suddenly decreased with ca. 100 °C negative spikes. In our conclusion by discussions [11], lower temperature hydrogen (D) gas in lower peripheral region of RC near oil-inlet would have blown up suddenly to make up-stream of colder convection gas flow. In the 4th day of PNZ10rr #1-4 run, TC4 temperature drew chaotic oscillation with smaller negative spikes and higher repetition as shown in Fig.4.



Fig.4; Evolution of data in the 4th day of PNZ10rr #1-4 run.

Inside temperatures in RC (upper left display) evolved very flat with average RC temperature of ca. 410 °C. The equilibrium temperature by the zirconia beads calibration run with [140, 95] W heater input was 322 °C. Excess thermal power is estimated as 86.6 W. Because of H(D)-gas turbulence effect under strong local AHE, excess thermal power levels have been underestimated by TC1, 2, 3 temperatures, but fortunately calorimetry by RTDav values was not visibly distorted [10, 11]. In this work, we have adopted excess thermal power data by RTDav (average RC temperature). In Fig.5, we show example of comparison of excess thermal power data between RTDav and TC1 adoptions. Because of the downward distortion of TC1 temperature correlating to TC4 chaotic oscillation, excess thermal powers by RTDav draw over 80 W that is reliable. Data by TC1 fluctuated around 40W, while data by RTDav increased up smoothly to saturated value over 80 W and continued for 5 days run (Monday to Friday).



Fig.5; Comparison of rise-up data of excess thermal powers by RTDav and TC1 for PNZ10rr #1-6 run

Bwteen ET (elevated temperature) runs, we turned off heaters [W1, W2] in the period of Friday to Monday. In every ET runs from Monday, we have observed generation of significant excess thermal power rise-up and similar TC4 chaotic oascillations. The AHE phenomenon is now very repeatable/reproducible, both for PNZ10-type with D-gas and CNZ7-type with H-gas (as shown later). Generated excess thermal power levels were near steady for several days, and switched on/off by heater on/off in controlable way. We show detail in the following.

To show the significant enhancement of AHE (anomalous heat effect) by the recalcination treatment of PNZ10r sample, data of PNZ10r #1-2 run [120, 80] (10, 11) is copied in Fig.6. Please remark on excess thermal power by RTDav. In rise-up, peak power exceeds 30 W but it decreases to rather flat value of ca. 16 W. By heating with [120, 80] watts, D-gas was desorbed to saturate at ca. 0.5 D-mol. Heat hump happened under larger D-desorption rate. Since large positive heat generation by desorption cannot be conceived by known chemical reactions, this data is already anomalous.

To be compared with it, we show data by PNZ10rr #1-2 run [120, 80] in Fig.7. Near 75 W steady excess thermal power was generated by this third calcined sample. Comparing with the cae of PNZ10r #1-2 run, we have got 4.7 times enhancement of excess thermal power level by the PNZ10rr #1-2 run. It is interesting to see that AHE of PNZ10rr #1-2 happened under D-absorption mode (saturating to ca. 0.2 D-mol absorption), which was endothermic D-absorption under heating up. Initial D-

absorption runs at RT (room temperature), PNZ10r absorbed more D-mol than PNZ10rr, by unknown change of nano-composite Pd-Ni islands to be studied further.



Fig.6; Copy of rise-up data of PNZ10r #1-2 run [10, 11]



Fig.7; Rise-up data of PNZ10rr #1-2 run (nominal) with [120, 80]

In Fig.8, generation of steady excess thermal power of 85 W level is shown by the succeeding ET runs with [140, 95] heating condition.



Fig.8; Repeatable and steady generation of excess thermal power by PNZ10rr sample

Average RC temperature made very steady evolution with ca. 410 °C, while TC4 temperature at central position of upper flange of RC made sporadic/chaotic oscillations by the gas turbulence effect. We may recognize that the chaotic TC4 oscillation is an indication of strong AHE in RC. Excess thermal powers were generated under the saturation state of D-desorption (ca. 0.05 D-mol).

In Fig.9, we show steady generation of excess thermal power for PNZ10rr sample after the second baking [10, 11] treatment.



Fig.9; Generation of excess thermal power for PNZ10rr #2-2 and #2-4 runs

AHE happened under slow D-absorption mode, in the case of PNZ10rr #2-2, and level of excess thermal power over 70 W increased slowly according to the decrement of D-absorption rate (due to endothermic absorption). AHE by PNZ10rr #2-4 generated steady excess thermal power of ca. 84 W. We found that the baking treatment did not make significant enhancement of excess thermal power, although it was effective for PNZ10r cases [10, 11]. Chaotic oscillation of TC4 temperature was taking place.

In Table-3, we summarize data of excess thermal power and RC average temperature by PNZ10, PNZ10r and PNZ10rr runs.

Run ID: Nominal	Heater Input (W)	Wex (W/kg); PNZ10	Wex (W/kg); PNZ10r	Wex (W/kg); PNZ10rr	RC Av-Temp (°C); PNZ10	RC Av-Temp (°C); PNZ10r	RC Av-Temp (°C); PNZ10rr
#1-2	[120, 80]	5	47.3	168	280	301.3	360
#1-4	[140, 95]	4	95	198	310	366	409
#2-2	[120, 80]	10		175	306		362
#2-4	[140, 95]	14	77	200	342	357	410
#3-2	[120, 80]	8		177	298		362
#3-4	[140, 95]	18	124	196	348	379	408
		sample weight: 1kg	sample weight: 0.45 kg	sample weight: 0.438 kg			

Table-3; Summary results of AHE enhancement for PNZ10-type samples with D-gas

Observed excess thermal power levels in average were 10, 86 and 186 W/kg-sample for PNZ10, PNZ10r and PNZ10rr, respectively with deuterium-gas. The enhancement of AHE power was largest by the second calcination, and was still large by the third calcination. We need to try the forth calcination to see further trend of AHE enhancement. Accordingly, average RC temperatures increased by the calcination and baking treatments. The effect of baking looks saturating for the third calcination sample runs. The AHE power level reached at 200 W/kg-sample level.

We have repeatedly reported [1-11] that observed level of excess thermal power was too large to be explained by chemical reactions which happens by exchange of atomic and molecular orbital electrons with small energy (less than a few eV per hydrogen or other atom, for instance). In this work, we have also obtained data of specific reaction energy per D-atom transfer as shown in Fig.10. Under long-lasting excess thermal power of near 90 W for nearly a month (190 MJ of total heat), we observed evolution of specific reaction energy reaching 100 keV/D-transfer at maximum.



Fig.10; Evolution of data of specific reaction energy per D-atom by PNZ10rr ET runs

We conceive that only a portion of transferred D-atoms was attributed to some unknown new condensed matter nuclear reactions (theoretical candidate is the CCF/TSC model [13, 14, 15]). Therefore, real specific reaction energy must be much larger to be over several MeV/D level as nuclear reaction level. As excess thermal power is taking place under flat D-transferred state (after saturation of either absorption or desorption of D-gas), we have conceived that 4D/TSC or 4H/TSC like cluster formation rate on surface catalytic sites of binary metal nano-islands is of key factor to enhance the effect.

#### 3-2 Heat Generation by CNZ7rr and H-Gas

We used 340g of third calcined sample of CNZ7rr plus 1011 g of filler zirconia beads to set up in RC. Oxidation rate by re-calcination was only 1.9%, but color of powder changed from grey to light brown by the re-calcination. Light hydrogen gas (H-gas) was used for AHE generation experiments, in similar way as PNZ10rr runs.

In Fig.11 we show the first ET run CNZ7rr #1-2-1 with [120, 80] W heating. About 70 W excess thermal power was obtained after saturation of H-absorption (0.4 H-mol). The chaotic oscillation of TC4 temperature happened similarly as the cases of PNZ10rr runs. We did only one day operation for CNZ7rr #1-2-1 run, and cooled to RT by making [0, 0] heating. Next day we started to run CNZ7rr #1-2-2 with [120, 80] W heating. The rise-up data of CNZ7rr #1-2-2 is shown Fig.11. We obtained excess thermal power level of ca. 70 W, namely same with that by CNZ7rr #1-2-1. AHE level is quite repeatable/reproducible, while AHE happened under the state after H-







Fig.11; ET run by one day after the initial ET run, CNZ7rr #1-2-2



Fig.12; One week data of AHE by CNZ7rr #1-2-2 run

In Fig.12, we show AHE data for 4 days run of CNZ7rr #1-2-2. Evolution of ca. 70 W excess thermal power is very steady. Chaotic oscillation of TC4 temperature evolved sporadically. The AHE continued after H-desorption saturated at the level of 0.07 H-mol. We are discussing that small fluctuation (in one minute averaged data plot) of desorbed H-gas level might have important information of frequent small change of H-gas in/out on surface of Cu-Ni nano-islands as mesoscopic catalyst sites where TSC formation is thought [13, 14]. We need precise and accurate measurement of gas pressure for that end.



FIG.13; 5 days long run of CNZ7rr #1-4 with [140, 95] W heating

In Fig.13, we show AHE data by 5 days long run of CNZ7rr #1-4.

Steady excess thermal power level over 80 W was observed under the H-gas desorption-saturated mode. Averaged RC temperature exceeded 400 °C. TC4 oscillation was sporadic as seen in other cases.



Fig.14; CNZ7rr #2-2 run, after the second baking treatment

In Fig.14, we show AHE data by CNZ7rr #2-2 run, after the second baking of sample. Similar level of ca. 70 W excess thermal power was obtained, comparing with the case of CNZ7rr #1-2-2. However, AHE took place under slow H-absorption mode, in this case. We compare results of rise-up data between CNZ7rr #1-2-1 and CNZ7rr #2-2, in Fig. 15. Rise-up of excess thermal power appeared with about 30 min delay for CNZ7rr #2-2, while the rise-up was faster for CNA7rr #1-2-1. Probably, larger endothermic H-absorption by CNZ7rr #2-2 is attributable to the slower excess power rise-up.

Finally, we show a baking data for CNZ7rr in Fig.16. Before baking, CNZ7rr sample retained ca. 0.76 H-mol, which corresponds to 0.5 H/Ni loading ratio. As we know 1.0 (full O-sites occupation)-3.0 (full O+T sites occupation) may be attained in Ni-core Pd (or Cu)-incomplete shell nano-islands [4] at RT, present observation of AHE excess thermal power evolution in rather steady level is considered to have been taking place under the non-saturation state of H-loading in Ni core at ET runs. We may conceive that optimum dynamic H-gas in/out flux on surface of binary nano-islands is of good condition for sustaining enhanced excess thermal power generation.

Summary table of enhancement effect of excess thermal power by re-calcination and baking treatments for CNZ7, CNZ7r and CNZ7rr samples is given in Table-4.



Fig.15; Comparison of rise-up data between CNZ7rr #2-2 run, after the second baking treatment, and CNZ7rr #1-2-1



Fig.16; Display of rise-up data for baking treatment of CNZ7rr #2-0

Enhanced feature of excess thermal powers by re-calcination is in average, 11, 117 and 226 W/kg-sample for CNZ7, CNZ7r and CNZ7rr, respectively with light hydrogen gas. The enhancement was slightly larger for CNZ7-type sample with H-gas than that of PNZ10-type samples with D-gas. The reason will be elucidated in future studies. Over 200 W/kg level and weeks lasting excess heat generation is now possible by using less expensive materials of Cu and Ni with conventional hydrogen gas with modest H-gas pressure (0.1-0.5 MPa) as 300-400 °C of RC temperature. It is very encouraging data source towards our target of industrial products development by the MHE energy [1-4] as radiation-less, high energy density and portable energy generation source.

Run ID: Nominal	Input W)	Wex (W/kg); CNZ7	Wex (W/kg); CNZ7r	Wex (W/kg); CNZ7rr	RC Temp (°C); CNZ7	RC Temp (°C); CNZ7r	RC Temp (°C); CNZ7rr
#1-2	[120, 80]	(152) (short burst)	96	219	(382 at burst)	336	358
#1-4	[140, 95]	12	110	245	336	383	405
#2-2	[120, 80]	6.8	118	214	295	346	357
#2-4	[140, 95]	14	126		359	392	
#3-2	[120, 80]	8.6	115		298	345	
#3-4	[140, 95]	13	137		349	392	
		sample weight: 1kg	sample weight: 0.505 kg	sample weight: 0.34 kg			

Table-4; Summary results of AHE enhancement for CNZ7-type samples with H-gas

## **VI SUMMARY AND CONCLUDING REMARKS**

Repeated re-calcination is effective to enhance sustainable excess thermal power by the interaction of Ni-based binary nano-composite metal powder with H (or D)-gas.

Baking treatment between elevated temperature runs is effective to enhance excess thermal power for the second re-calcination, but the enhancement has saturated for the third re-calcination.

To eliminate the gas turbulence effect for calorimetry, condition of homogeneous temperature in sample region will be tested to enhance more AHE.

Excess thermal power reached at the level of 200 W/kg-sample continuing for several weeks or more, by the elevated temperature interaction of either D-gas or H-gas and Ni-based binary nano-composite powders supported in zirconia flakes.

Further extension study towards application of industrial clean portable primary thermal energy source is encouraging.

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## Start-up of Metal Crystal confinement Fusion Reactor

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Abstract "Metal crystal confinement fusion reactor" is a reactor that utilizes the mechanism of generating large excess heat generated from the Pd cathode after completion of heavy water electrolysis experiments. A mechanism of the excess heat generation is the fusion chain reaction, which is called the " combustion reaction" among the three reactions reported by the authors in the "Nuclear Fusion Mechanism in Metal Crystals [1]". The reactor was named "Metal crystal confinement fusion reactor," meaning that high-energy deuterons and  $\alpha$ -particles were confined by the crystal channeling phenomenon, causing fusion unique to metals.

As an example of confirming the intermediate product of the fusion chain reaction, there is a report on SIMS analysis of a Pd cathode in which the formation of <sup>6</sup>Li was confirmed [2]. As an example of confirming the production of  $\alpha$ -ray and <sup>4</sup>He as final products, there is a report of an experiment in which electricity is supplied to an  $\alpha'$ -phase Pd coated with gold on one side to release deuterium [3]. The author believes that the transmutation experiment [4] that the number of nucleons increased by an integral multiple of the  $\alpha$  nucleus shows that the  $\alpha$ -rays pass through the 140nm stack to reach the transmuted nucleus, causing fusion unique to metal.

The basic form of the "Metal crystal confinement fusion reactor" is a metal heating element in which <sup>6</sup>Li is impregnated into a low-strain metal and a deuterium gas is put in the reactor. Then, the metal heating element is activated by irradiating it with  $\alpha$  rays or the like. Estimation of the <sup>6</sup>Li appropriate content was performed by comparing the SIMS analysis result [2] of the Pd cathode for which the formation of <sup>6</sup>Li was confirmed with the SIMS analysis result of the standard sample.

The experimental reactor used here was a pure Pd plate sample doped with <sup>6</sup>Li of 180keV on the surface as a metal heating element. Although no fever was confirmed, generation of gamma rays and neutron burst for 1.5h were confirmed. The generation of such a nuclear reaction product is evidence that a fusion chain reaction has occurred since a trace source of only 8000Bq of  $\alpha$ -ray was used.

**Index Terms---** Fusion Reactor, Fusion Chain Reaction, Metal Crystal, Channeling, Palladium, Deuterium, <sup>6</sup>Li, 2α reaction, Combustion Reaction, Heat after Death, Excessive heat, Metal Crystal confinement,

1. "Metal crystal confinement fusion reactor" uses the principle of "Heat after death ".

"Heat after death" refers to the phenomenon in which a Pd cathode generates heat for

a long time after no current flows in an electrolysis experiment of heavy water. Figure 1 was published in the paper of "Heat after Death" by S. Pons and M. Fleischmann, shows that the temperature of the Pd cathode was high for about 3 hours after the electrolyte was evaporated and no current flowed in the electrolysis experiment [5].



Fig. 1 The temperature-time curve for a cell being driven to boiling showing also the initial part of the cooling curve - 2 mm length Pd cathode polarized in 0.1M LiOD in D<sub>2</sub>O; final cell current: 500mA [5].

In Japan, Mizuno experienced "Heat after death". Mizuno wrote in his book that 100g of Pd electrode at least generated 114MJ of heat from the Pd electrode for at least 12days from April 25 to May 7, 1991 after the electrolysis experiment [6].

Figure 2 shows the design of the sealed cell used in the electrolysis experiment of Mizuno [6]. At the center is a Pd cathode, and at the top is a catalyzer for returning generated deuterium gas and oxygen gas to heavy water. In both experiments, heavy water

in which LiOD was melted was used as the electrolyte.



Fig. 2 Design of sealed cell [6].

## 2. Fusion chain reaction

According to the theory of "Nuclear Fusion Mechanism in Metal Crystals [1]" published in the JCF18 by the author, in the "transmutation experiment [3]", "ignition reaction", "combustion reaction" and "transmutation reaction" had been occurred in metal crystals, and the transmutation had occurred. And "Heat after death" is caused by the "combustion reaction". The "combustion reaction" occurs when light nuclei represented by  $\alpha$ -rays become high-energy charged particles and enter a Pd crystal having a low deuterium concentration where channeling easily occurs.

First, due to the channeling phenomenon of the Pd metal crystal, the high-energy charged particles accurately pass through the center of the sparse part of the crystal lattice. This increases the probability that the high-energy charged particles are scattered
by deuterium nuclei contained in the metal crystal. Due to these scattering, the reaction direction of the high-energy charged particles changes, and the nuclei of deuterium receive kinetic energy and become high-energy deuterons. The high-energy charged particles repeat scattering until they lose their energy, resulting in the production of many high-energy deuterons.

Further, the probability of fusion increases due to the channeling phenomenon of the Pd metal crystal. In addition, since Pd metal is conductive, free electrons absorb fusion energy as kinetic energy or phonons and cause "mild fusion" in which no gamma rays or neutrons are emitted.

First, the high-energy deuterons cause "mild fusion" with the nuclei of <sup>2</sup>H between the Pd lattices impregnating the Pd metal, producing <sup>4</sup>He as shown in the following equation.

(a)  ${}^{2}H(d) {}^{4}He$ 

After <sup>4</sup>He accumulates between the Pd lattices, the <sup>4</sup>He nuclei undergo "mild fusion" of high-energy deuterons, producing <sup>6</sup>Li as shown in the following equation.

(b)  ${}^{4}\text{He}(d) {}^{6}\text{Li}$ 

After <sup>6</sup>Li accumulates between the Pd lattices, the <sup>6</sup>Li nuclei undergo "mild fusion" of high-energy deuterons. At this time, <sup>8</sup>Be is not formed because unstable, and two  $\alpha$  rays are directly generated as in the following equation.

(c)  ${}^{6}\text{Li}(d, \alpha) \alpha$ 

These  $\alpha$  rays distribute energy by scattering to deuterium nuclei of interstitial atoms, and again generate many high-energy deuterons. Although not a nuclear reaction, this is represented by the following equation.

(d)  $\alpha$  (<sup>2</sup>H, d)  $\alpha$ 

A large number of high-energy deuterons are generated when the high-energy charged particles approach the nuclei of interstitial atoms with a high probability due to the channeling phenomenon of the crystal. The deuterons cause unique "mild fusion" within the metal with other interstitial nuclei. In this way, the above-described chain reaction of a-d occurs. The fusion chain reaction is a "combustion reaction", which is a reaction that generates "heat after death". <sup>4</sup>He and <sup>6</sup>Li are produced as intermediate products, and  $\alpha$  rays are produced as final products. When  $\alpha$  rays stop in Pd metal, they take away electrons from their surroundings, become <sup>4</sup>He atoms.

#### 3. Confirmation example <sup>6</sup>Li by combustion reaction

Figure 3 shows SIMS analysis data of Pd-5 cathode sample without heat generation and neutron detection during electrolysis by Okamura et al. [2]. The horizontal axis is

the distance from the electrode surface, and the vertical axis is the number of secondary ions of SIMS. Notice the upper two lines that show the secondary ion numbers for <sup>7</sup>Li and <sup>6</sup>Li. The Li isotope <sup>7</sup>Li / <sup>6</sup>Li ratio in nature is 92.5:7.5. Near the electrode surface, the 7Li / 6Li ratio is this ratio, however, at 50000Å (5µm), the <sup>7</sup>Li / <sup>6</sup>Li ratio changed to 1: 1. The portion deeper than 20000Å(2µm) from the surface clearly indicates that <sup>6</sup>Li had be generated.

Okamoto et al. show the results of SIMS analysis of five cathode samples with different electrolysis currents [2]. The samples other than Pd-5 have a trend of more deuterium and more Li [2]. The trend can be explained by considering that if an electrolytic current that impregnates a large amount of deuterium is applied to the Pd cathode during electrolysis, a large amount of Li will also be impregnated. However, only Pd-5 has a small amount of deuterium relative to the amount of Li, and the diffusion of Li progresses and impregnates deeply. This indicates that only Pd-5 has a history of being exposed to high temperatures because Pd emits deuterium and the diffusion rate increases at high temperatures. It has been reported that no neutrons and no heat generation were observed during electrolysis of the Pd-5 cathode, so it is presumed that the Pd-5 cathode was exposed to high temperatures after the electrolysis was completed. In other words, this increase of <sup>6</sup>Li can be considered to have been generated by "Heat after death".



Fig. 3 The typical examples of depth profiles observed by SIMS analysis [2].

4. Confirmation example of <sup>4</sup>He and  $\alpha$ -ray by combustion reaction

Figure 4 is a Pd sample diagram of the experiment of Yamaguchi et al., which is  $3.0 \text{cm} \times 3.0 \text{cm}$  (thickness = 1.0mm) [3]. One side of the Pd sample impregnated with a large amount of deuterium is coated with gold, so when electricity is applied, deuterium is released from the opposite side. After the experiment, the flat sample warps like a part of a sphere, with the gold-coated side inside. This is because Pd on the gold-coated side shrinks last. This shrinkage occurs because the  $\alpha'$  phase Pd impregnated with a large amount of deuterium transforms to the  $\alpha$  phase when exhaling deuterium.



Fig. 4 Pd sample after neutron burst and release of D<sub>2</sub> gas [3]

Figure 5 is a schematic diagram of the experimental apparatus by Yamaguchi et al. [3]. The gold-coated surface of the sample is on the lower side, and the charged particles emerging from the upper surface are detected by SSD.

Figure 6 summarizes the energy distribution of charged particles from four types of samples impregnated with gases with different mixing ratios of light hydrogen and deuterium by Yamaguchi et al. [3].  $\alpha$  particles of about 6 MeV, which are the final product of the fusion chain reaction, have been detected.



Fig. 5 Schematic diagram of the experimental equipment of Yamaguchi et al. [3]





Fig. 7 Mass spectrometry of the released gas with a nominal mass of 4

in a sample impregnated with pure deuterium gas [3]

Figure 7 shows mass spectrometric data of the nominal mass 4 of the gas released from the sample every 75 minutes [3]. At the beginning of the experiment, only deuterium gas was detected, but 4He gas was detected as early as 75 minutes. Since the fusion chain reaction first occurs in the  $\alpha$ -phase Pd with a low deuterium concentration near the deuterium releasing surface side, the time until <sup>4</sup>He gas release is considered to be short.

Over time, the amount of detection of hydrogen molecules HT by tritium and light hydrogen has increased, but these tritium and light hydrogen are the products of an "ignition reaction" that occurs when  $\alpha'$  phase Pd is deformed. I consider "ignition reaction" to be a kind of special nuclear reaction that occurs in metal, but the product is the same as the well-known DD fusion. The release is time consuming since it is produced in the  $\alpha$  'phase with a high deuterium concentration remote from the release surface. Yamaguchi et al. had also confirmed neutrons emitted [3] by the "ignition reaction."

#### 5. Transmutation example by $\alpha$ ray of combustion reaction

Figure 8 is a schematic diagram of a sample of a transmutation experiment performed by Mitsubishi Heavy Industries and a partially enlarged image of a cross section [4]. On the upper surface of a 1 mm thick pure Pd plate, a laminated structure of 5 layers of 2 nm CaO and 20 nm Pd is formed, and further thereon is a 40 nm Pd layer in which a transmutation material is embedded [4]. Since the upper surface of this sample is filled with D<sub>2</sub> gas and the lower surface is evacuated, deuterium permeates from the upper portion, passes through the sample, and is discharged from the lower surface.

By continuing the permeation of deuterium gas for 100 hours or more, Cs embedded in the surface undergoes transmutation, and transmutes to Pr, a rare substance on Earth.



Fig. 8 Schematic diagram and partial enlarged image of cross section of transmutation sample [4].

Table 1 summarizes the transmutation results of the transmutation experiment [4]. Each substance Cs, Ba, and W undergoing transmutation are transmuted so that the atomic number and mass number are increased by 2, 4, or 6 times that of deuterium nucleus (written as d). These are the result of the  $\alpha$  rays generated by the fusion chain reaction generated in the pure Pd plate part, passing through the 140 nm lamination, and causing mild fusion with the nuclei of these substances.

I YPICAL REACTIONS OBSERVED SO FAR							
Elements		Assumed Reactions					
Cs	4d	${}^{133}_{55}Cs \xrightarrow{4d(2\alpha)}_{59}{}^{141}_{59}Pr$					
Ba	6d	$^{138}_{56}Ba \xrightarrow{6d(3\alpha)}{150}_{62}Sm, ^{137}_{56}Ba \xrightarrow{6d(3\alpha)}{149}_{62}Sm$					
W	4d or 2d	${}^{182}_{74}W \xrightarrow{4d(2\alpha)}_{78} Pt,  {}^{186}_{74}W \xrightarrow{2d(\alpha)}_{76} Os$					

Table 1 Nuclear reactions confirmed in transmutation experiments [4].

#### 6. Basic configuration of metal crystal confinement fusion reactor

To reiterate, the true nature of " Heat after death " is the fusion chain reaction described above. Li is impregnated in the Pd cathode by electrolysis, and after the electrolysis is stopped, deuterium is released from the Pd cathode. Then, the chain reaction is started when high-energy charged particles enter a portion where Li and D have an appropriate concentration.

Figure 9 is a conceptual diagram showing a basic configuration of a "metal crystal confinement fusion reactor". The reactor should be started by placing a metal heating element (Pd) impregnated with <sup>6</sup>Li in the reactor, placing an  $\alpha$ -ray source near it, and injecting deuterium gas. There is a possibility that even if Pd impregnated with a small amount of deuterium is doped with a deuteron beam for a long time, the reactor may be activated. However, the fusion chain reaction does not start until <sup>4</sup>He accumulates by nuclear reaction and <sup>6</sup>Li accumulates by nuclear reaction. Therefore, I thought that the reactor would be possible to start up quickly by impregnating <sup>6</sup>Li in advance, and made this configuration.



Fig.9 Metal Crystal confinement Fusion Reactor

# 7. Estimation of <sup>6</sup>Li concentration at which combustion reaction becomes active

In order to realize the "metal crystal confinement fusion reactor", it is necessary to find appropriate <sup>6</sup>Li and D concentrations at which the "combustion reaction" occurs. If it is too thin, the chance of causing a reaction is reduced, and if it is too dense, the ion beam trajectory is disturbed and nuclear fusion does not occur. Although the D concentration can be changed in the experiment, it is necessary to know an appropriate concentration because <sup>6</sup>Li must be dissolved in the metal heating element in advance.

Therefore, I decided to refer to the <sup>6</sup>Li concentration at the site where the nuclear reaction is actively occurring in figure 3. However, since figure 3 is the data of the secondary ion amount of SIMS, it is necessary to convert to the <sup>6</sup>Li concentration. So, I decided to make a standard sample, measure the number of secondary ions in SIMS, and find a conversion factor for estimating the Li concentration.

However, the paper in which figure 2 is published does not describe the SIMS device or measurement conditions. If the SIMS measuring device, the type of primary ion, the amount of energy, and the like are different, the ratio of the amount of secondary ions changes by one digit or more. Then, looking for information on SIMS used by Okamoto et al., two years later Okamoto et al.'s paper showed that the SIMS equipment was CAMECA / France's IIMS-4S, the primary ion species was O<sub>2</sub><sup>+</sup>, and the primary ion acceleration was It was stated that it was 15.1 keV [7]. Furthermore, I contacted coauthor Odawara to confirm more detailed SIMS measurement conditions and that Pd in figure 3 is <sup>106</sup>Pd.

From this information, I prepared the following standard sample and decided to measure it under the SIMS measurement conditions shown below. The results are shown in figure 9.

Standard sample <sup>6</sup>Li ion implantation status

Sample metal:	7x7x1t, 99.9wt% pure Pd, 1000°C annealing for 1h
Ion species:	<sup>6</sup> Li
Energy:	180keV
Dose amount:	$2.30 \times 10^{15}$ /cm <sup>3</sup>
Beam current:	200eµA
Number of scans:	2018
Injection time:	3544.50sec

SIMS measurement Mode IMS-6f (Successor of IIMS-4S, CAMECA / France) Device:  ${\rm O_2}^+$ Primary ion species: Primary ion acceleration voltage: 15keV Sample stage potential: 4.5keV 10.5keV Secondary ion voltage: Positive Secondary ion polarity: Riser area: 150µm□ Analysis area: 60µmφ Mass resolution: normal



Fig.10 Depth profile observed by SIMS analysis of the standard sample.

The peak number of <sup>6</sup>Li secondary ions reached  $2.03 \times 10^{6}$  counts at a depth of  $0.34\mu$ m. From the dose and the accumulated count, the peak concentration at the point was estimated to be  $7.24 \times 10^{19}$ /cm<sup>3</sup>. From these values, a coefficient to be converted into a concentration was determined by the following equation.

$$7.24 \times 10^{19} / 2.03 \times 10^{6} = 3.57 \times 10^{13} \text{ [/counts /cm^3]}$$

The average amount of secondary ions of <sup>106</sup>Pd of the standard sample in figure 10 is  $8.72 \times 10^4$  counts. I read that the number of <sup>6</sup>Li secondary ions in the actively reacting region at a depth of 50000Å in figure 3 was 12.9 times <sup>106</sup>Pd. From these numerical values, the amount of <sup>6</sup>Li secondary ions at a <sup>6</sup>Li concentration that actively reacts can be obtained by the following calculation. Multiplying this by the coefficient gives the estimated concentration of <sup>6</sup>Li.

 $8.72 \times 10^{4} \times 12.9 = 1.125 \times 10^{6} \text{ [counts]} ---\text{Secondary ion amount}$  $1.125 \times 10^{6} \times 3.57 \times 10^{13} \text{ (coefficient)} = 4.012 \times 10^{19} \text{ [/cm^3]} ---^{6}\text{Li estimated concentration}$ 

Since the specific gravity of Pd is 12.023, the atomic density of Pd having a mass number of 106.43 is

$$12.023/106.43 \times 6.022 \times 10^{23} = 6.80 \times 10^{22} \text{ [/cm^3]}$$

Therefore, the molar concentration of <sup>6</sup>Li can be obtained as follows.

 $4.012 \times 10^{19}/6.80 \times 10^{22} = 0.059$  [mol%] ----Estimated mol concentration of <sup>6</sup>Li

I read that the number of <sup>7</sup>Li secondary ions in the region where no reaction occurred at a depth of 20000Å in figure 3 was 147 times as large as <sup>106</sup>Pd. From the 147 times, similarly, the <sup>7</sup>Li concentration and mol% at which the reaction does not occur can be calculated as follows.

$$8.72 \times 10^{4} \times 147 \times 3.57 \times 10^{13} = 4.57 \times 10^{20} \text{ [/cm^{3}]} \qquad --- ^{7}\text{Li estimated concentration} \\ 4.57 \times 10^{20} / 6.80 \times 10^{22} = 0.67 \text{ [mol\%]} \qquad --- \text{ Estimated mol concentration of }^{7}\text{Li}$$

8. Making a metal heating element A 99.95% Pd plate was used as a base for the metal heating element. If possible, I want to add <sup>6</sup>Li uniformly at a concentration of  $4.012 \times 10^{19}$ /cm<sup>3</sup>, which reacts actively, but the method has not been established. Therefore, I aimed at the peak concentration of  $4.012 \times 10^{19} \times 3 = 1.20 \times 10^{20}$  [atm/cm<sup>3</sup>], which was three times that of the above, and dosed 6Li of 180 keV at  $5.1 \times 10^{15}$  atm/cm<sup>2</sup>.

Figure 11 shows a calculation result of the <sup>6</sup>Li concentration distribution of the heating element Pd sample when the dose amount is set to  $5.1 \times 10^{15}$  atm/cm<sup>2</sup>. The two light blue straight lines are drawn at  $4.012 \times 10^{19}$ /cm<sup>3</sup> and  $4.57 \times 10^{20}$ /cm<sup>3</sup> calculated above. The area between these two lines is likely to act a nuclear reaction, but the thickness is only less than  $0.5\mu$ m, so it is not certain that the resulting particles will stay in this area. Therefore, the possibility that the chain reaction can be started is not high.



Fig. 11 Calculation result of <sup>6</sup>Li concentration distribution of heating element Pd sample

9. Experimental Reactor with Samples and Sources

Figure 12 shows the appearance of the experimental reactor. Figure 13 shows a Pd sample of  $\varphi$ 76 in the reactor and an  $\alpha$ -ray source placed on the <sup>6</sup>Li-doped surface.



Fig. 12 Experimental reactor of Metal Crystal Confinement Fusion Reactor



Fig. 13  $\phi76Pd$  sample and  $\alpha\text{-ray}$  source

#### 10. Experimental results



Fig. 13  $\gamma$ -ray survey meter

Fig. 14 Neutron survey meter

Figure 13 shows the gamma-ray survey meter and figure 14 shows the neutron survey meter used this time.

This time, the 5th experiment, whose startup was confirmed by the emission of radiation, used 99.95% pure Pd annealed at 1300 ° C for 1 hour in the atmosphere used in the 4th experiment. In the fourth start-up experiment, <sup>6</sup>Li was doped at  $9.81 \times 10^{14}$ /cm<sup>2</sup>, so <sup>6</sup>Li was further doped at  $5.0 \times 10^{15}$ /cm<sup>2</sup>.

Start baking at room temperature at 6:00 on January 22, 2019, raise the temperature to 75 ° C on January 23, 8:00, and continue baking, January 24, 2019 at 10:31, gamma ray 0.400 $\mu$ Sv/h, and thereafter gamma rays of 0.100 $\mu$ Sv/h or more were confirmed for about 1.5h continuously. The gamma dose at the experimental site is usually 0.020 to 0.050  $\mu$ Sv/h, and occasionally a high value may come out momentarily. At this time, since it came out continuously, I think that it is the result of the continuous nuclear reaction in the reactor. I think that the start during baking was the sample in which deuterium gas had already been introduced in the fourth experiment.

At 15:33, the valve on the pump side was closed and baking was stopped. Then, after adding 0.258cc of deuterium gas in 5 times, at 19:38 on January 24, 2019, the  $\gamma$ -ray exceeded 0.100 $\mu$ Sv/h and started to drop, and then the neutron survey meter suddenly mitted a continuous sound. The neutron survey meter was not designed to give an alarm, so I understood that the beeping sound when neutrons were captured was emitted continuously. Normally, the neutron survey meter shows a value of about 0.00-0.05 $\mu$ Sv/h at this experimental site, but at this time I saw the display of  $3.40\mu$ Sv/h. (Some values could not be confirmed, and in fact, it seems that more values came out.) When confirmed later, as shown in figure 15, the correction count recorded 3513.5, which is about 1000 times the background value. Since this is a count of 5 minutes, it is likely that most of the neutrons were actually emitted within a few seconds of the continuous sound.

Since then, small gamma-ray bursts and neutron bursts have been confirmed many times. For example, at 9:03 on January 26, a neutron display of  $16\mu$ Sv/h was visually observed, and the correction count at this time was 100.5/5minutes. At 17:35 on January 27, a neutron display of  $3.02\mu$ Sv/h was visually observed, and the correction count at this time was 37.5/5minutes.

													A DESCRIPTION OF THE OWNER OWNER OF THE OWNER OW		
~13	記錄目時	線量率	単位	調整	単位	線量率	ページ	単位	精算	単位	積算 1-7	トレント・周期	補正	電池電 圧(V)	高圧測 定值(Y)
34	2019/01/24 18:49:51	0.03	uSv/h	0.13	uSv	0.003	34	area/h	0.013	nren	ON	300	4.0	7.70	315
34	2019/01/24 18:54:51	0.02	uSv/h	0.13	USY	0.002	34	area/h	0.013	area	ON	300	1.0	7.70	315
35	2019/01/24 18:59:51	0.02	uSv/h	0.14	USV	0.002	35	area/h	0.014	area	ON	300	2.0	7.64	315
35	2019/01/24 19:04:51	0.02	uSv/h	0.14	USY	0.002	35	area/h	0.014	area	ON	300	2.0	7.64	315
35	2019/01/24 19:09:51	0.02	uSv/h	0.14	USY	0.002	35	area/h	0.014	nren	ON	300	1.5	7.84	315
35	2019/01/24 19:14:51	0.01	uSv/h	0.14	uSv	0.001	35	area/h	0.014	nres	ON	300	0.5	7.64	315
35	2019/01/24 19:19:51	0.02	uSv/h	0.14	USV	0.002	35	area/h	0.014	area	ON	300	2.0	7.84	315
38	2019/01/24 19:24:51	0.01	uSv/h	0.14	USV	0.001	36	area/h	0.014	area	ON	300	0.0	7.58	315
36	2019/01/24 19:29:51	0.07	uSv/h	0.15	USV	0.007	36	area/h	0.015	nren	ON	300	6.5	7.58	315
36	2019/01/24 19:34:51	0.03	uSv/h	0.15	USV	0.003	36	area/h	0.015	area	ON	300	1.5	7.58	315
38	2019/01/24 19:39:51	0.11	uSv/h	4.52	) USV	0.011	36	area/h	0.452	area	ON	300	(3513.5)	7.58	315
38	2019/01/24 19:44:51	0.05	uSv/h	4.52	USV	0.005	38	area/h	0.452	nren	ON	300	4.5	7.58	315
37	2013/01/24 19:49:51	0.02	uSv/h	4.52	USV	0.002	37	area/h	0.452	area	ON	300	1.0	7.44	315
37	2019/01/24 19:54:51	0.02	usy/h	4.53	USY	0.002	37	nrea/b	0.453	Bren	CAL	200	54		

Fig.15 Data during neutron burst

After that, the reactor was re-manufactured in a different location to provide a protective wall, and a reproduction experiment was performed. As a result, at 10:14 on October 31, 2019, the neutron survey meter indicated  $0.49\mu$ Sv/h. When the peak value of the background was measured at the location over two days, it was  $0.080\mu$ Sv/h for gamma rays and  $0.20\mu$ Sv/h for neutrons. So, I thought it was due to a reaction. However, when the background was measured over the next four days this year, peaks of  $0.340\mu$ Sv/h for  $\gamma$ -rays and  $0.90\mu$ Sv/h for neutrons were confirmed, so it cannot be said that the reaction was confirmed at the location.

#### 11. Summary and Inference of Experimental Results

- I estimated that the concentration of <sup>6</sup>Li in Pd that causes active fusion chain reaction is about 0.059 mol% based on the SIMS data of Okamoto et al. [2] and the SIMS measurement results of my standard sample.
- 2) Heat generation in the experimental reactor could not be confirmed, but it is considered

that the startup of the experimental reactor could be confirmed by detecting gamma rays and neutron beams.

3) In the above fusion chain reaction, gamma rays and neutron rays should not be emitted originally. I believe that the generation of these radiations was confirmed because unintended nuclear reactions would occur if the fusion chain reaction continued.

Although the energy value of  $\gamma$ -rays could not be specified, if the  $\gamma$ -ray was the 511.5 keV  $\gamma$ -ray confirmed in the transmutation experiment [4], it was due to the annihilation of energetic positrons, so it would be thought that a nuclear reaction in which positrons is emitted occurred.

Pd sample of January was 99.95% pure Pd annealed at 1300 ° C for 1 hour in air, and Pd sample of October was 99.95% pure Pd baked at 1250 ° C for 2.5 hours in vacuum. Therefore, I think that the reaction of <sup>1</sup>H (p, e+ ve) <sup>2</sup>H frequently occurred in the Pd sample in January, but it did not occur in the October.

I think that the neutron generation is caused by the  ${}^{2}H$  (d, n)  ${}^{3}He$  reaction the same as in normal DD fusion when the deuterium becomes excessive.

5) The background of  $\gamma$ -rays and neutrons was measured over a total of 6 days, and the peak value was obtained. As a result, the  $\gamma$ -rays were  $0.340\mu$ Sv / h, about 15 times the normal value, and the neutrons were  $0.90\mu$ Sv / h, about 50 times the normal value, was observed. Therefore, it should be noted that, especially in the case of neutrons, a peak dose of several tens of times the normal dose does not guarantee that the neutrons have come out of the experimental apparatus.

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## Computer Simulation of Transition Energy of H atoms in Cu, Ag and Au Metal Lattices

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Abstract: Two or more nuclei (the proton or the deuteron) of H or D atoms would condense so that nuclear fusion and/or nuclear transmutation could occur in metals. H or D atoms would gather to generate high density cohesion state and cause some trigger reactions on or inside the metal surface during the diffusion process prior to the condensation of p or d. The differences of total energy (transition energy) when an H atom transited between O sites and T sites or between O sites and other O sites in Cu, Ag and Au metal lattices following Al metal lattice were estimated by computer simulation. As a result, the total energy of H atom on O sites in Cu metal lattice with the surface and volume relaxation became lower periodically about  $0.3 \sim 0.5$  eV than that on T sites or near them according to the lattice periodicity when H atoms had entered O sites. However, the energy differences between O sites and T sites or near them in Ag metal lattice became smaller than that in Cu, and that in Au metal lattice became unclear similar to the last study in Al metal lattice. This suggests that H atoms can stay on O sites in Cu metal (be occluded), but hardly stay on O sites or T sites in Ag, Au and Al metal. Further, when H atoms transit from O sites to other O sites, they need excess energy about 0.3~0.5 eV. A few thermal electrons in Cu metal could get energy more than 0.5 eV to collide with these H atoms. The possibility was recently reported that neutrinos could, although with a low probability, result from inelastic collisions of particles of a substance (electrons, ions, neutral atoms) during their thermal motion, which could cause low energy nuclear reactions (LENR) due to weak interactions.

Keywords: computer simulation, NEB method, transition energy, hydrogen, copper, silver, gold

#### 1. Introduction

There have been a lot of studies about excess heat and generation of elements which seem to be related to nuclear fusion and nuclear transmutation. Two or more nuclei (the proton (p) or the deuteron (d)) of hydrogen (H) or deuterium (D) atoms would condense so that these nuclear fusion and/or nuclear transmutation could occur in metals, and H or D atoms would gather to generate high density cohesion state while simultaneously cause some trigger reactions on or inside the metal surface during diffusion process prior to the condensation of p or d to get nuclear fusion and/or nuclear transmutation. As for a method, differences of total energy (transition energy) were estimated by computer simulation, when an H atom transited between tetrahedral (T) sites and octahedral (O) sites or O sites and other O sites in copper (Cu), silver (Ag) and gold (Au) of face centered cubic (FCC) metal lattices following aluminum (Al) metal lattice <sup>1)</sup>. Calculations were carried out by using Nudged Elastic Band (NEB) method on a computer simulation program Quantum ESPRESSO (opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization) of the first principle molecular dynamics, imposed periodic boundary conditions on a slab-structural calculation unit of (0 0 1) surface of Cu, Ag and Au metal lattices.

As a result, in the first instance, the total energy of an H atom on the surface of each Cu, Ag or Au metal lattice decreased when some H atoms had entered O sites with the surface and volume relaxation which optimized the metal atoms of lattice points freely to move except the lowest layer of the calculation unit cell, which would mean that H atoms can stay on the surface or around the voids of Cu, Ag and Au metals. Furthermore, the total energy of an H atom on O sites in Cu metal lattice became lower periodically about  $0.3 \sim 0.5$  eV than that on T sites or near them according to the lattice periodicity with the surface and volume relaxation which optimized the metal atoms. However, the energy differences between O sites and T sites or near them in Ag metal lattice became smaller than that in Cu metal lattice. This would mean that H atoms easily stay on O sites far inside the surface of Cu metal (be occluded), but hardly stay there of Ag, Au and Al metal (be not occluded), and furthermore, that H atoms need excess energy about  $0.3 \sim 0.5$  eV when they transit from O sites in Cu metal.

Recently, a paper was published that neutrinos could, although with a low probability, result from inelastic collisions of particles of a substance (electrons, ions, neutral atoms) during thermal motion of electrons with an energy more than 0.5 eV which appeared in the noticeable fraction of energy distribution of electrons with average energy more than about 0.1 eV (a temperature of about 1000 K), which could cause low energy nuclear reactions (LENR) of absorption of electrons by nuclei due to weak interactions <sup>2</sup>). Applying this theory to Cu metal lattice, we could expect the mentioned LENR would occur at room temperature (average energy about 0.03 eV) when some electrons around H atoms, which transit the energy barrier of about  $0.3 \sim 0.5$  eV or a bit smaller by such as tunneling effects between O sites and other O sites, were excited to the energy more than 0.1 eV. This LENR would probably occur not

only in Cu metal but also nickel (Ni) or palladium (Pd) metal whose energy barrier for the transition of H atoms was higher to easily occlude them. However, this LENR will hardly occur in Ag, Au and Al metal of lower energy barrier between O sites.

The movement of H or D atoms in metals is considered to be essential to the LENR in electrolysis, gas permeation, gas occlusion, etc. The phosphorus (P) generation rate under vibratory agitation of magnesium (Mg) chloride aqueous solution was found out to be the same in the order of magnitude as the reaction rate in the published paper.

#### 2. Calculations

#### 2.1 Method, Hardware and Software Used for Calculation

As for the simulation of transition of H atom in metal lattices, differences of total energy (transition energy) arisen from transition of H atom between two sites in the metal lattice were investigated by using NEB <sup>3</sup>) method on a computer simulation program Quantum ESPRESSO (Ver. 5) <sup>4</sup>) based on the density functional theory of the first principle molecular dynamics on a personal computer (PC) which had 4 cores / 8 ways CPU with 32 GB main memory. This program was working on the molecular computation support system program Winmoster<sup>TM</sup> which ran NEB method and assisted in exchanging element types and changing atomic coordinates, and in immediately showing lattice structures of metals and outputting graphics of calculated total energy, etc. <sup>5</sup>).

#### 2.2 Calculated Metal lattices

Calculations were carried out by imposing periodic boundary conditions on slab-structural calculation unit of  $(0\ 0\ 1)$  surface Cu, Ag and Au of FCC metal lattices which was composed of 2x2x2 layered conventional simple cubic cells of four metal atoms and had 25 Å thick vacuum layer. It is necessary to calculate similarly on Ni and Pd metal lattices, but not established for lack of proper pseudo potential for them.

NEB method finds minimum energy path between known reactants by optimizing a number of intermediate images along the reaction path. By using NEB method, total energy on the path of H atom in slab-structural calculation units was calculated as follows.

< No H atom has entered O sites: >

For two cases of a) Fixing the all metal atoms of lattice points (without the surface and volume relaxation) and b) Fixing the metal atoms of lowest layer lattice

points (with the surface and volume relaxation),

- Between on-top sites, bridge sites and hollow sites on the metal surface,
- Between T sites or O sites inside the metal surface and the sites mentioned above,
- Between T sites and O sites each other mentioned above.

< Some H atoms have entered the other O sites: >

Three H atoms per calculation unit cell are concentration lower than 0.1 to Cu, Ag or Au atoms and concentration locally about 0.5.

For two cases of a) Fixing the all metal atoms of lattice points (without the surface and volume relaxation) and b) Fixing the metal atoms of lowest layer lattice points (with the surface and volume relaxation),

• Between the same sites mentioned at (1).

In these calculations, the case of "b) Fixing the metal atoms of lowest layer lattice points (with the surface and volume relaxation)" in "< Some H atoms have entered the other O sites: >" seems to be actual states of metals which occlude H atoms.

For an example,  $(0 \ 0 \ 1)$  surface slab-structural calculation unit of the Cu metal lattice is shown in Fig. 1.



The rectangular solid surfaces represent the boundaries of a supercell calculation unit that defines a Cu metal lattice with periodic boundary conditions in all three directions. The atoms in the lower portion of  $2 \times 3.36148$  (lattice constant of Cu) Å width supercell fill the entire supercell in the x and y directions, but vacuum of empty space is left above the atoms of  $2 \times 3.36148$ Å thickness in the top portion of the supercell with 25Å total width and fill the entire supercell in z direction.

Fig.1 (0 0 1) surface slab-structural calculation unit of Cu metal lattice

Calculated sites were named as illustrated in Fig. 2. These sites were selected for an H atom to get into the Cu metal lattice from a surface bridge or a hollow site to a T site or an O site and deeply between T sites and O sites or between O sites and other O sites by repeated transitions. For the NEB calculations, the short distances between sites on the surface were divided into three equal paths (four steps) and long distances between T sites and O sites or between O sites and other O sites inside it were divided into six equal paths (seven steps) or twelve equal paths (thirteen steps). The H atom on each site of the surface was set away from it about 1 Å optimized to the perpendicular or depth direction (Z axis).



Fig. 2 Sites naming of (0 0 1) surface slab-structural calculation unit

O sites named O1, O2, O3, O4, O5, O6 and T sites named T1, T2, T3 are represent by " $\downarrow$ " and "×", and on-top sites OT1, OT2, bridge site B1 and hollow site H1 are also represented.

#### 3. Results and Discussion

Calculations were carried out in Cu, Ag and Au of FCC metal lattices following to Al metal lattice.

#### 3.1 No H atom has entered O sites

Total energy was calculated when an H atom transited between on-top sites, bridge sites and hollow sites on the metal surface, between those sites and T sites or O sites and between those T sites and O sites or between O sites and other O sites inside the metal surface of the  $(0\ 0\ 1)$  surface slab-structural calculation unit of Cu metal lattice, as an example, shown in Fig. 1 and named as Fig. 2.

Fig. 3, Fig. 4 and Fig. 5 shows the total energy in Cu, Ag and Au metal lattices respectively. Broken lines indicate calculations for transitions between B1-H1-T1-O1-T2-O3-T3 sites of a) Fixing the all metal atoms of lattice points (without the surface and volume relaxation), solid lines indicate those of b) Fixing the metal atoms of lowest layer lattice points (with the surface and volume relaxation), and long broken lines indicate calculations for transitions between O1-B4/T2-O3-B6/T3 sites of the same case b).

In all metal lattices, the total energy with or without the surface and volume relaxation became lowest when an H atom was placed in bridge sites and hollow sites on the metal surface. The total energy with the surface and volume relaxation decreased when an H atom was placed in H1-H2 (near T1) sites of metal surface (left hand side of solid lines of lower graphs in Fig. 3, Fig. 4 and Fig. 5). Moreover, the total energy with the surface and volume relaxation became lower as a whole about  $0.2 \sim$ 0.6 eV,  $0.3 \sim 0.6 \text{ eV}$  and  $1.5 \sim 1.7 \text{ eV}$  in Cu, Ag and Au metal lattice (center or right hand side of solid lines and long broken lines of lower graphs in Fig. 3, Fig. 4 and Fig. 5) than that without the surface and volume relaxation respectively (center or right hand side of broken lines of upper graphs in Fig. 3, Fig. 4 and Fig. 5).

Without the surface and volume relaxation, the total energy of an H atom placed in O sites became lower periodically about  $0.3 \sim 0.6$  eV,  $0.2 \sim 0.5$  eV and  $0.2 \sim 0.4$  eV than that placed in T sites or hollow sites of Cu, Ag and Au metal lattice according to the periodicity of each metal respectively (center or right hand side of broken lines of upper graphs in Fig. 3, Fig. 4 and Fig. 5). On the other hand, with the surface and volume relaxation, the total energy of an H atom placed in O sites became lower periodically about  $0.3 \sim 0.5$  eV,  $0.2 \sim 0.4$  eV and  $0.1 \sim 0.2$  eV than that placed in T sites or near them (B4, B6) of Cu, Ag and Au metal lattice according to the periodicity of each metal respectively (center or right hand side of solid lines and long broken lines of lower graphs in Fig. 3, Fig. 4 and Fig. 5).



Fig. 3 Total energy of an H atom in Cu metal lattice when no H atom has entered

Fine character and [] indicate sites inside the surface, H2, H4 and H6 indicate near T sites Broken lines indicate total energy without the surface and volume relaxation, and solid lines and long broken lines indicate those with the surface and volume relaxation respectively.



Fig. 4 Total energy of an H atom in Ag metal lattice when no H atom has entered

Fine character and [] indicate sites inside the surface, H2, H4 and H6 indicate near T sites Broken lines indicate total energy without the surface and volume relaxation, and solid lines and long broken lines indicate those with the surface and volume relaxation respectively.



Fig. 5 Total energy of an H atom in Au metal lattice when no H atom has entered

Fine character and [] indicate sites inside the surface, H2, H4 and H6 indicate near T sites Broken lines indicate total energy without the surface and volume relaxation, and solid lines and long broken lines indicate those with the surface and volume relaxation respectively.

#### 3.2 Some H atoms have entered the other O sites

In the case of three H atoms having entered O sites (O2, O4, O6), similar to "3.1 No H atom has entered O sites", total energy was calculated when an H atom transited between on-top sites, bridge sites and hollow sites on the metal surface, between those sites and T sites or O sites and between those T sites and O sites or between O sites and other O sites inside the metal surface.

Fig. 6, Fig. 7 and Fig. 8 shows the total energy in Cu, Ag and Au metal lattice respectively. Broken lines indicate calculations for transitions between B1-H1-T1-O1-T2-O3-T3 sites of a) Fixing the all metal atoms of lattice points (without the surface and volume relaxation), solid lines indicate those of b) Fixing the metal atoms of lowest layer lattice points (with the surface and volume relaxation), and long broken lines indicate calculations for transitions between O1-B4/T2-O3-B6/T3 sites of the same case b).

In all metal lattices, similar to "3.1 No H atom has entered O sites", the total energy with or without the surface and volume relaxation became lowest when an H atom was placed in bridge sites and hollow sites on the metal surface. The total energy with the surface and volume relaxation decreased when an H atom was placed in H1-H2 (near T1) sites of metal surface (left hand side of solid lines of lower graphs in Fig. 6, Fig. 7 and Fig. 8). Moreover, the total energy with the surface and volume relaxation became lower as a whole about  $0.8 \sim 1.5$  eV,  $0.8 \sim 1.5$  eV and  $2.8 \sim 3.5$  eV in Cu, Ag and Au metal lattice (center or right hand side of solid lines and long broken lines of lower graphs in Fig. 6, Fig. 7 and Fig. 8) than that without the surface and volume relaxation respectively (center or right hand side of broken lines of upper graphs in Fig. 6, Fig. 7 and Fig. 8).

Without the surface and volume relaxation, the total energy of an H atom placed in O sites became lower periodically about  $0.8 \sim 0.9$  eV,  $0.7 \sim 0.8$  eV and  $0.4 \sim 0.5$  eV than that placed in T sites or hollow sites of Cu, Ag and Au metal lattice according to the periodicity of each metal respectively (center or right hand side of broken lines of upper graphs in Fig. 6, Fig. 7 and Fig. 8). On the other hand, with the surface and volume relaxation, the total energy of an H atom placed in O sites became lower periodically about  $0.3 \sim 0.5$  eV,  $0.1 \sim 0.2$  eV and  $0.0 \sim 0.1$  eV than that placed in T sites or near them (B4, B6) of Cu, Ag and Au metal lattice according to the periodicity of each metal respectively (center or right hand side of solid lines and long broken lines of lower graphs in Fig. 6, Fig. 7 and Fig. 8).



Fig. 6 Total energy of an H atom in Cu metal lattice when three H atoms have entered
Fine character and [] indicate sites inside the surface, H2, H4 and H6 indicate near T sites
Broken lines indicate total energy without the surface and volume relaxation, and solid
lines and long broken lines indicate those with the surface and volume relaxation respectively.



Fig. 7 Total energy of an H atom in Ag metal lattice when three H atoms have entered Fine character and [] indicate sites inside the surface, H2, H4 and H6 indicate near T sites Broken lines indicate total energy without the surface and volume relaxation, and solid lines and long broken lines indicate those with the surface and volume relaxation respectively.



Fig. 8 Total energy of an H atom in Au metal lattice when three H atoms have entered Fine character and [] indicate sites inside the surface, H2, H4 and H6 indicate near T sites Broken lines indicate total energy without the surface and volume relaxation, and solid lines and long broken lines indicate those with the surface and volume relaxation respectively.

#### 4. Discussion

Metal atoms on or near inside the surface or around the voids would be actually in the state with the surface and volume relaxation, and those far inside the surface would be also actually in the state without the surface and volume relaxation. Then an H atom would enter the metal as follows related to the above computer simulation.

< When almost no H atom has entered the metal: >

(1) An H atom stays on or near inside the surface of the metal (left hand side of solid lines of lower graphs in Fig. 3, Fig. 4 and Fig. 5).

(2) It enters inside the surface of the metal (center or right hand side of solid and long broken lines of lower graphs in Fig. 3, Fig. 4 and Fig. 5).

(3) It enters far inside the surface of the metal (center or right hand side of broken lines of upper graphs in Fig. 3, Fig. 4 and Fig. 5).

(4) It stays around the voids of the metal (center or right hand side of solid and long broken lines of lower graphs in Fig. 3, Fig. 4 and Fig. 5 the same as (2)).

< When many H atoms have entered the metal: >

(5) Another H atom stays on or near inside the surface of the metal (left hand side of

solid lines of lower graphs in Fig. 6, Fig. 7 and Fig. 8).

(6) It enters inside the surface of the metal (center or right hand side of solid and long broken lines of lower graphs in Fig. 6, Fig. 7 and Fig. 8).

(7) It enters far inside the surface of the metal (center or right hand side of broken lines of upper graphs in Fig. 6, Fig. 7 and Fig. 8).

(8) It stays around the voids of the metal (center or right hand side of solid and long broken lines of lower graphs in Fig. 6, Fig. 7 and Fig. 8 the same as (6)).

When H atoms had entered the other O sites, the total energy of the H atom placed in O sites far inside the surface of Cu metal lattice with the surface and volume relaxation became lower about  $0.3 \sim 0.5$  eV than that placed in T sites or near them according to the periodicity of the metal (center or right hand side of solid and long broken lines of lower graphs in Fig. 6) relevant to (7) mentioned above. On the other hand, this decrease in the total energy in Ag metal lattice became small (center or right hand side of solid and long broken lines of lower graphs in Fig. 7), and that in Au metal lattice became unclean (center or right hand side of solid and long broken lines of lower graphs in Fig. 8) similar to the last study in Al metal lattice <sup>1)</sup>. This would mean that H atoms easily stay in O sites far inside the surface of Cu metal (be occluded), but hardly stay there of Ag, Au and Al metal (be not occluded), and furthermore, that H atoms need excess energy about  $0.3 \sim 0.5$  eV or a bit smaller by such as tunneling effects when they transit the energy barrier between O sites in Cu metal.

#### 4.1 Relation to theory

Recently, a paper was published that a pair of electron neutrino-antineutrinos of very small mass believed not to exceed 0.28 eV could, although with a low probability, result from inelastic collisions of particles of a substance (electrons, ions, neutral atoms) during thermal motion of electrons with an energy more than 0.5 eV which appeared in the noticeable fraction of energy distribution of electrons with average energy more than about 0.1 eV (a temperature of about 1000 K), which could cause rearrange nucleons with absorption of electrons by nuclei, the LENR due to weak interactions<sup>2</sup>). This paper reported that most of those reactions would be caused when metals are at a temperature 1000 K or more and the reaction rate would be estimated about 2 x  $10^{16}/\text{sec/cm}^3$  at 2000 K.

However, it would be considered that metal atoms at lattice points could not cohere together and react on each other by generated electron neutrino because metals of Cu, Ag, Au and Ni, Pd, etc. are in solid state at 2000 K or less and hardly to move. Furthermore, this computer simulation showed that H atoms could diffuse between O sites near inside the surface or around the voids of Cu metal with excess energy about  $0.3 \sim 0.5$  eV or a bit smaller, the average energy would be more than about 0.1 eV (a temperature of about 1000 K) by such as collisions or vibrations in some way, and they could not cohere together and react on each other by generated electron neutrino.

Therefore, the following reactions would be caused in metals of low temperature less than 1000 K and be related with the reported estimation of 2000 K in the paper.

(1) Transition or diffusion of H/D atoms in metal

In electrolysis, H/D gas permeation or occlusion, or under vibratory agitation, H/D atoms are occluded in Cu, Ni or Pd metal, etc., and then transit or diffuse with kinetic energy about  $0.3 \sim 0.5$  eV.

(2) Collision of thermal electrons with transiting or diffusing H/D atoms

Thermal electrons in Cu, Ni or Pd metal, etc. collide with transiting or diffusing H/D atoms with kinetic energy about  $0.3 \sim 0.5$  eV, and then get excess energy to generate locally thermal electrons of temperature 2000 K (energy of about 0.2 eV).

(3) Neutrino pair production and LENR by neutrino

Each electrons of energy more than 0.5 eV which appeared in the noticeable fraction of energy distribution of electrons with temperature locally more than 2000 K collide with the lattice metal atoms or H/D atoms and electrons to produce a electron neutrino-antineutrino pair, probably emitting a photon, in Cu, Ni or Pd metal, etc. Then the neutrino pairs could cause the LENR due to weak interactions.

#### 4.2 Relation to Experiments

It would be considered that H/D atom related to generation of excess heat (nuclear fusion) or other elements (nuclear transmutation) in the electrolysis of light or heavy water, deuterium gas permeation or occlusion, or under vibratory agitation of electrolyte.

Under the vibratory agitation, it would be supposed that some spherical bubbles were formed and collapsed near the pressurized surface of vibration blade when it moved periodically <sup>6</sup>). The water cage cluster of nucleus in the collapsing spherical bubble would be pressed by water molecules which flowed into the collapsing spherical bubble to form the high density water cage cluster of double cubic ice mutually insert each other, and the high density water cage clusters would probably collide randomly on the surface of vibration blade. Then, H/D atoms and O atoms or other metal atoms which compose the large mas of high density water cage cluster would collide with the surface of vibration blade one after another in a short time. The

light H/D atoms would collide prior to the other heavy atoms with the surface of vibration blade, and would be squeezed into it by them, and on the other hand, they would accumulate on it. The theory mentioned in "4.1 Relation to theory" could be applied to the H/D atom cohesion state and accumulation of other heavy atoms which were formed on or near inside the surface or around the voids of vibration blade metal.

It had been reported that 1,900 mg/L phosphorus (P) was generated by the vibratory agitation from 30 L of 2,900 mg/L magnesium (Mg) chloride aqueous solution using five vibration blades of about 20 x 5 cm area and about 5  $\mu$ m thickness in about 6 hours. This P generation rate became about10<sup>17</sup>/sec/cm<sup>3</sup> that was the same in the order of magnitude as the reaction rate in the paper mentioned above. The ratio of P generation through the vibratory agitation would be considered to efficiently increase because the Pd coating thickness of metal surface of vibration blade was slightly equivalent to the de Broglie wavelength of electron neutrino of energy about 0.1 eV.

The LENR due to the electron neutrino would occur on or near inside the surface or around the voids of metal under vibratory agitation, and in the electrolysis or gas permeation, and furthermore perhaps on or near the joint surface of different metals in the electrolysis or gas permeation, etc., where H atoms and other atoms densely gather within the reaction area of the de Broglie wavelength of electron neutrino which probably causes the LENR of absorption of electrons by nuclei due to weak interactions.

#### 5. Summary

In order to find out some trigger reactions out or nside the metal surface during the diffusion process prior to the condensation of p or d to get nuclear fusion and/or nuclear transmutation, we estimated the differences of total energy (transition energy) when an H atom transited between sites in Cu, Ag and Au metal lattices following Al metal lattice by computer simulation. As a result, the total energy of an H atom on the surface of each Cu, Ag or Au metal lattice with the surface and volume relaxation decreased, which would mean that H atoms can stay on the surface or around the voids of Cu, Ag or Au. Furthermore, the total energy of an H atom on O sites in Cu metal lattice became lower periodically about  $0.3 \sim 0.5$  eV than that of on T sites or near them according to the lattice periodicity with the surface and volume relaxation when H atoms had entered O sites. However, this energy difference in Ag metal lattice became unclear similar to the last study in Al metal lattice. That suggests H atoms can easily

stay in O sites far inside the surface of Cu metal (be occluded), but they hardly stay there of Ag, Au and Al metal (be not occluded). Furthermore, that suggests H atoms which transit the energy barrier between O sites need about  $0.3 \sim 0.5$  eV or a bit smaller, or says that they have the excess kinetic energy of that value.

Recently, the paper was published that neutrinos could, although with a low probability, result from inelastic collisions of particles of a substance (electrons, ions, neutral atoms) during thermal motion of electrons with an energy more than 0.5 eV which appeared in the noticeable fraction of energy distribution of electrons with average energy more than about 0.1 eV, which provably cause the LENR due to weak interactions. Applying this theory to Cu metal lattice, we could expect the LENR occur at room temperature when some electrons around H atoms which transit the energy barrier of about  $0.3 \sim 0.5$  eV between O sites are excited to more than about 0.1 eV. This LENR would occur not only in Cu metal but also in Ni or Pd metal whose energy barrier for the transition of H atoms is higher to occlude them. In the relation to experiments, the P generation rate under vibratory agitation of Mg chloride aqueous solutions is the same in the order of magnitude as the reaction rate in the paper.

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## Deuterium Desorption Experiment Using Surface-Coated Pd Foil with a Fine-Structured Interface

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#### <u>Abstract</u>

A deuterium desorption experiment was performed using a Pd-Ni composite metal sample in which the interface was processed using an ultra-short pulse laser. From the results of the experiment, the characteristic phenomenon of short-period temperature fluctuations, observed in our previous study, was not observed. However, we found a feature of the Pd-Ni composite metal sample in deuterium diffusion, which may cause a non-uniform local density of deuterium in the sample. We have also tested individual Pd and Ni samples and their composite membrane to measure the hydrogen diffusion behavior in them. The hydrogen diffusion coefficient was found to be significantly enhanced over a certain temperature range for Ni coated with Pd membranes.

#### 1. Introduction

Excess heat evolution has been observed in deuterium absorption/desorption process for nano-composite-particle of Pd-Ni-Zr sample. Kitamura and Takahashi et al. reported excess heat evolution in the deuterium absorption and desorption process in Pd-Ni composite nanoparticles [1-3]. Iwamura et al. successfully reproduced this phenomenon in their own apparatus [4, 5]. In addition, excess heat and helium generation have been reported in the deuterium desorption process in a Pd foil coated with Au and metal oxide (MnO/SiO) membrane by Yamaguchi et al. [6]. These results have been considered to be a new physics process involving a low-energy nuclear reaction, although their mechanisms have not been understood yet.

We have conducted deuterium absorption and desorption experiments using Pd-based metal complex samples, which were fabricated by depositing a metal membrane, such as Ni, Ag, Ti, and Zr, onto a Pd foil. In particular, in the sample of Pd coated with Ni or Zr membrane with a fine-structure at the interface, we sometimes observed a short-period fluctuation in temperature, which indicated that a prompt deuterium diffusion occurred bidirectionally between the Pd foil and the membrane [7, 8]. We have

not found significant excess heat generation so far [8]. However, such a characteristic temperature behavior resulting from the peculiar deuterium diffusion might be due to the sample conditions such as "composite metal" and "fine-structured sample". Understanding this unique phenomenon might help explain the origin of the excess heat observed in some experiments.

In this study, we attempted to use an ultra-short pulse laser to produce a well-controlled fine-structure on the sample interface, with the expectation of improving the reproducibility of the occurrence of an anomalous temperature behavior and to understand the reactions that occur in the sample. In addition, deuterium diffusion in a metal membrane, especially with a hetero-structure, can clarify the distinct phenomenon observed. For this purpose, we have extracted the diffusion coefficient of hydrogen for the membranes of Pd, Ni, and their composite.

#### 2. Experiment

#### 2.1 Sample preparation

An ultra-short pulse laser was used to etch one of the surfaces of a Pd foil (10 mm  $\times$  10 mm  $\times$  0.1 mm) with a lattice pattern. Table 1 lists the specifications of the laser and the processing conditions. The laser beam diameter was approximately 20–30  $\mu$ m, which is defined as the diameter at which the intensity at the center of the Gaussian beam becomes  $1/e^2$ . After surface etching, the sample was ultrasonically cleaned with acetone for 15 min to remove organic impurities, followed by annealing at 900 °C for 11 h for homogenizing the crystal structure. After this, the metal impurities were removed by aqua regia. Finally, a 200-nm-thick Ni membrane was deposited onto the laser-processed surface by Ar<sup>+</sup> ion beam sputtering.

 Table 1. Specifications of the ultra-short pulse laser

Maker/Model	Light Conversion Co. /Pharos					
Laser medium	Yb:KGW crystal					
Oscillation center wavelength	1028 nm					
Power	400 mW					
Pulse width	260 fs					
Pulse repetition frequency	100 kHz					
Lattice pitch width	10 µm					

Figure 1 shows the surface morphology obtained using atomic force microscopy (AFM) of the samples prepared using two different etching methods, (a) after etching with  $Ar^+$  ion beam (Fig. 1(a)), as in our past study, and (b) etching using an ultra-short pulse laser (Fig. 1(b)). The raster size was 10 µm x 10 µm for each image. Many projections with a height of approximately 200 nm can be observed in the case of etching with  $Ar^+$  ion beam in Fig. 1(a). However, in the case of etching with a laser, we do not observe a distinct shape or a regular pattern.



**Fig. 1.** Surface morphology plots obtained by an AFM of Pd foil after etching it with (a) an Ar ion beam (left), and (b) ultra-short laser pulse (right)

The sample surface was also analyzed by transmission electron microscopy (TEM) in order to evaluate its microscopic structure. It should be noted that a Pt layer was deposited onto the sample to prevent the sample from being damaged during the TEM analysis. Figure 2 shows the TEM images of the sample etched by  $Ar^+$  ion beam at different magnifications. A semi-spherical shape of size 50–200 nm was found. Figure 3 shows the TEM images of the sample processed by the laser. A protruding structure with a width of approximately 100 nm was observed. However, there was no significant difference as compared to the sample prepared by the  $Ar^+$  beam etching process.



Fig. 2. TEM images of the sample etched by the  $Ar^+$  ion beam



Fig. 3. TEM images of the sample processed by laser

#### 2.2 Deuterium loading

The fabricated Pd-Ni complex samples were exposed to the deuterium gas at 5 atm for  $\sim$ 24 h to load deuterium. The weight of the sample was measured before and after loading, and the loading ratio (D/Pd) was calculated from the difference in the weights. Figure 4 shows the loading ratio for the different samples. The average values of the ratios have also been indicated. We do not see any dependence of the loading ratio on the two etching methods used.



Fig. 4. Deuterium loading ratio (D/Pd) for the different samples

#### 2.3 Deuterium desorption experiment

In the desorption experiment, the sample was placed into a cylindrical chamber of volume 1400 cm<sup>3</sup>, equipped with a turbo-molecular pump (TMP) used for evacuation (~10<sup>-4</sup> Pa). The pressure in the chamber was measured using an ionization vacuum gauge. A DC power supply was used for supplying a constant current to the sample via chrome clips in the chamber to stimulate deuterium out-diffusion from the sample. The chamber was evacuated by the TMP during the desorption experiment. The sample temperature was measured using a thermocouple with an accuracy of  $\pm 1$  °C. A schematic of the experimental setup is shown in Fig. 5. We assume that the DC power was supplied only to the Ni side because the clips are in contact with the Ni membrane only through the Au electrode.



Fig. 5. Schematic of the experimental setup



Fig. 6. (a) Temporal changes in the temperature, voltage, and pressure in the deuterium desorption process carried out for ~ 20 h. In (b) is plotted the variation of these three parameters for the initial 3 h of the experiment

#### 2.4. Results and Discussion

The temporal changes in the temperature, pressure, and voltage during a  $\sim 20$  h deuterium desorption experiment is shown Fig. 6(a). The temperature was observed to increase sharply just after applying the current and fluctuated for around 1 h afterwards. Beyond this, it was observed to remain more or less constant. The voltage also fluctuated till around 1 h after applying the current, concurrent to the temperature fluctuation. The pressure increased immediately after applying the current, which indicates deuterium out-diffusion from the sample to the chamber, and then gradually decreased due to evacuation. We have not seen the short-period temperature fluctuations that were observed in our previous experiment using a sample processed by an Ar<sup>+</sup> ion beam. The surface condition of the sample obtained by laser etching is apparently different from that by an Ar<sup>+</sup> beam etching and it was supposed be ineffective in inducing the characteristic deuterium diffusion which might cause the short-period temperature fluctuations.

Other than the absence of the short-period temperature fluctuations, we have observed a correlated variation in the temperature, pressure, and voltage in the initial period of the experiment. This has been shown in Fig. 6(b), which is an enlarged view of Fig. 6(a), corresponding to the results for the initial 3 h of the experiment. The characteristics of the experimental results can be roughly classified into a "significant pressure increase" and a "significant voltage decrease." The pressure was observed to increase approximately 2 min after applying the current and increased steeply until approximately 5 min. The pressure change,  $\Delta P$ , in this period was observed to be  $+0.2 \times 10^{-3}$  Pa, and the voltage change,  $\Delta V$ , was  $\sim -0.2$  mV. Furthermore, the gradient of
the temperature change per unit time, (dT/dt), was observed to increase when the pressure curve showed a smooth decrease.



**Fig. 7.** Temperature, chamber pressure, and applied voltage as a function of time for the Pd-Ni sample with fine-structure by  $Ar^+$  beam.

**Fig. 8.** Temperature, chamber pressure, and applied voltage as a function of time for the Pd-Ni sample without any fine-structure.

From these results, we can assume that in the desorption process, the deuterium in the Pd foil diffuses into the Ni membrane, since deuterium desorption from Pd is an endothermic reaction, and is then desorbed to the chamber. The electrical resistivity of the sample decreases due to the decreasing deuterium density in the sample, which results in a decrease in the voltage applied to the sample. In addition, the deuterium out-diffusion from the sample to the chamber increases the partial pressure in the chamber.

Further, we have observed that the voltage decreased significantly ( $\Delta V = -1.9 \text{ mV}$ ) at about 20 min and continued to decrease for 8 min beyond that. In this period, a simultaneous increase in the temperature and a decrease in the pressure ( $\Delta P = -0.4 \times 10^{-3}$  Pa) were observed. It was thus assumed that the process of deuterium desorption from the Ni membrane to the chamber was exothermic. It has also been assumed that the evacuation capability of the TMP is much more effective than the quantity of the deuterium diffused from the sample. This might explain why the pressure in the chamber decreased a little during this period.

Figure 7 shows the results of the deuterium desorption experiment using the Pd-Ni sample with a fine-structure interface etched by an  $Ar^+$  ion beam. A short-period temperature fluctuation is thought to be a distinct behavior for the sample. Figure 8 shows the result of the deuterium desorption experiment using the Pd-Ni sample without fine-structure. In both samples, a similar behavior in the initial period of the experiment, as compared to that seen in the laser-processed sample, was observed.

Although we have not performed sufficient number of experiment runs even with other types of sample, this behavior might be due to the effect of a combination of Pd foil and Ni membrane. Further study is needed to clarify the process of the behavior observed.

### 3. Hydrogen diffusion experiments

#### **3.1 Sample preparation**

A 24 mm  $\times$  24 mm  $\times$  0.50 mm glass substrate was cleaned with acetone, Semicoclean (manufactured by Furuuchi Kagaku), and ultrapure water for 10 min each. Thereafter, water was completely blown off by the Ar gas. Yttrium (Y), palladium (Pd), nickel (Ni), and aluminum nitride (AlNx) membranes were formed onto the glass substrate by Ar ion beam sputtering. Because the light transmittance of Y changes on hydrogenation, the evolution of hydrogen diffusion can be visually observed. In addition, an AlNx membrane with the ability to block hydrogen was formed on the uppermost portion to observe diffusion in Pd or Ni in the horizontal direction. In this experiment, four types of samples were prepared. Figures 9(a)-(d) show the schematic view of each sample; (a) the Y-Pd-AlNx sample is a single-layer Pd film sample in which a Pd membrane is formed between Y and AlNx. (b) The Y-Pd-Ni-AlNx sample is a Pd-Ni multi-layer film sample in which a Pd membrane is formed between Y and AlNx and a Ni membrane is formed as a hydrogen inlet. (c) The Y-Ni-AlNx sample is a Ni single-layer film sample in which a Ni membrane is formed between Y and AlNx. (d) The Y-Ni-Pd-AlNx sample is a Ni-Pd multi-layer film sample in which a Ni membrane is formed between Y and AlNx and a Pd membrane is formed as a hydrogen inlet.



Fig. 9. A cross sectional view of the samples used for the hydrogen diffusion experiment

#### 3.2 Experiment

The experimental procedure was as follows:

- 1) The sample was mounted on the ceramic heater inside a plastic chamber with the Y-side visible.
- 2) The chamber was evaluated until the pressure inside reached  $\sim 1.0 \times 10^{-2}$  Pa.
- The sample was heated at 60 °C / 150 °C / 300 °C (tested at different temperature conditions).
- 4) Hydrogen gas was introduced at a pressure of 1 atm.
- 5) The time evolution of the hydrogenation on the Y side was observed for 24 h using a video camera, and the hydrogen diffusion coefficient of the membrane was calculated.

A schematic of the experimental setup for the hydrogen diffusion experiment is shown Fig. 10.



Fig. 10. Experimental setup used for investigating the hydrogen dissolution behavior in the samples

The diffusion coefficient was calculated by measuring the length of the edge of the hydrated region, which can be identified from the change in the color of Y, that occurs in a certain time period. The diffusion coefficient was measured at three locations: upper, middle, and lower (as indicated in Fig. 11), since the diffusion speed was different depending on the position.



**Fig. 11**. Image showing the method used for identifying the hydrogen diffusion in the membrane.

#### 3.3 Results and Discussion

# **3.3.1** Calculation of the hydrogen diffusion coefficient using the Arrhenius equation

Generally, the hydrogen diffusion coefficient, D, in a bulk metal is a function of the temperature, T, and is given by the Arrhenius equation:

$$D = D_0 \exp\left(\frac{-E_a}{\mathrm{kT}}\right) \quad (\mathrm{m}^{2/\mathrm{s}}) \qquad (1)$$

where  $D_0$  and  $E_a$  are the pre-exponential factor and the activation energy, respectively, and are constants that are defined for each metal type. T is the absolute temperature and k is the Boltzmann constant. The pre-exponential factors and activation energies for Pd and Ni used for different temperature ranges are given in Table 2 [9], and the diffusion coefficient curves have been plotted in Fig. 12.

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	Temperature	$D_0$ (× 10 <sup>-7</sup>	$E_a(eV)$			
	range (K)	m <sup>-</sup> /s)				
Pd	230-760	2.9	0.23			
Ni	220-330	1.8	0.40			
	385-620	6.7	0.41			

**Table 2.** Pre-exponential factors and the activation energies for Pd and Ni used for different temperature ranges

In the case of bulk Pd (Fig. 12(a)),  $E_a = 0.23$  eV and  $D_0 = 2.9 \times 10^{-7}$  m<sup>2</sup>/s were assigned for temperatures between 230 and 760 K. Similarly, in the case of bulk Ni (Fig. 12(b)),  $E_a = 0.40$  eV and  $D_0 = 1.8 \times 10^{-7}$  were assigned for temperatures between 220 and 330 K, while  $E_a = 0.41$  eV and  $D_0 = 6.7 \times 10^{-7}$  m<sup>2</sup>/s were assigned for temperatures between 385 and 620 K. From the plots, the hydrogen diffusion coefficient in bulk Pd at 333 K is  $0.96 \times 10^{-10}$  m<sup>2</sup>/s while that in bulk Ni at 333 K is 1.6 to  $4.2 \times 10^{-13}$  m<sup>2</sup>/s.



**Fig. 12.** Hydrogen diffusion coefficients of (a) Pd and (b) Ni calculated from the Arrhenius equation.

#### **3.3.2 Results and Discussion**

The hydrogen diffusion coefficients in the single-layer Pd membrane sample, Pd-Ni multi-layer membrane sample, and bulk Pd at each temperature are summarized in Table 3. Some conditions have not yet been tested (blank cells in the table). The bulk value was obtained from the Arrhenius curves shown in Fig. 12.

Fig. 9) at different testing temperatures.						
Sample type	60 °C	150 °C	300 °C			
(a)Pd(100nm)	$2.4 \sim 21.6 \times 10^{-10}$	-	-			
(b)Pd(100nm)	$5.8 \times 10^{-10}$					
with Ni(100nm)	5.8 ~ 10	-	-			
(c)Ni(50/100nm)	$\leq 6.7 \times 10^{-13}$	-	$1.8 \sim 3.6 \times 10^{-8}$			
(d)Ni(100nm)	$2.2 - 7.0 \times 10^{-10}$	$\sim 10^{-10}$	1.4~1.8 × 10 <sup>-8</sup>			
with Pd(100/20nm)	2.5~7.9 × 10	$\leq 0.7 \times 10^{-3}$				
Bulk Pd	$0.96 \times 10^{-10}$	$5.3 \times 10^{-10}$	$2.7 \times 10^{-10}$			
Bulk Ni	$1.6 \sim 4.2 \times 10^{-13}$	$8.7 \times 10^{-12}$	$1.7 \times 10^{-10}$			

**Table 3.** Diffusion coefficients (in m<sup>2</sup>/s) for each sample type (prepared as shown in Fig. 9) at different testing temperatures.

For the samples containing the Pd membrane, samples (a) and (b) (i.e., the samples in Figs. 9(a) and 9(b)), the diffusion coefficient was found to be several times larger than the bulk Pd sample. This is considered that one of the characteristics of the metal membrane for hydrogen diffusion. In addition, we had expected that a composite structure of Pd and Ni can bring about a peculiar diffusion behavior. However, there is no significant difference in the diffusion coefficient between samples (a) and (b). From the results for samples (c) and (d) (i.e., the samples in Figs. 9(c) and 9(d)) at 60 °C, the hydrogen diffusion coefficient in the Ni membrane was found to be enhanced by placing a thin Pd layer on the area where hydrogen was introduced and it was 1000 times larger than that of the bulk Ni sample. This property may cause the unique behavior observed in our desorption experiments for a Pd sample that is coated by a Ni membrane. However, hydrogen diffusion was observed in both samples (c) and (d) at 300 °C, but significant difference was not confirmed between them. Because the Pd membrane peeled off at 150 °C, we could not measure hydrogen diffusion.

This study is still undergoing and we need further experiments under different sample conditions to clarify the hydrogen diffusion coefficient in membrane is enhanced as well as its temperature dependence.

#### 4. Summary

To improve the reproducibility and to understand the mechanism of the periodic temperature fluctuation in the deuterium desorption test that we had observed in a previous experiment, we examined a Pd-Ni complex sample having a fine-structure interface processed with an ultra-short pulse laser. From the result, it is found that there is no distinct behavior observed so far. In addition, it has been observed that the temperature, voltage applied to the sample, and pressure in the chamber showed a correlated variation during the early period of the desorption experiment. We have assumed the following scenario from the observed results: a relatively large amount of deuterium was released from the Pd side first followed by a relatively small amount of deuterium released from the Ni membrane side. This behavior was observed for the sample even without fine structure at the interface between Pd and Ni. We now assume that directional deuterium diffusion occurs gradually in the Pd-Ni composite and the deuterium density in the sample is nonuniform locally. However, we had been observed the changes in temperature, voltage applied to the sample, pressure in the chamber which similar above mentioned in Pd foil sample without metal membrane and any fine-structure. We will need to confirm the reproducibility by further conducting deuterium absorption and desorption experiments using Pd-Ni samples and conclude the effect of the combination of Pd and Ni by investigate past experimental results.

We also investigated the hydrogen diffusion coefficient for the bulk Pd and Ni samples and their composite membrane. From the investigation, the hydrogen diffusion coefficient was found to be much enhanced for Ni coated with a Pd membrane at 60 °C. This could be because Pd might be providing a catalytic effect in hydrogen dissolution as compared to other metals and it is more effective at low temperatures. Further systematic experiments to measure the hydrogen diffusion behavior will clarify the properties of Pd-metal composites.

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# Elemental Analysis for Elucidation of the Anomalous Heat

# **Generation Phenomena**

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#### Abstract

We have performed the anomalous heat generation experiments using a nano-sized metal multilayer composites on Ni under absorption of  $H_2$  gas. Some samples, which were composed of Ni, Cu and CaO or  $Y_2O_3$  thin films on bulk Ni, generated heat bursts phenomena and anomalous excess energy. It is necessary to elucidate the reaction mechanism and the conditions to cause these phenomena in a nano-sized metal multilayer composite. We carried out to analyse each sample using scanning electron microscope (SEM)/ energy dispersive X-ray spectroscopy (EDX) and time of flight secondary ion mass spectrometry (TOF-SIMS) to understand about the surface states, depth profiles and mass spectra for before- and after-experiment samples.

As a result, the surface states of the samples which were subjected to heating up to  $500-900^{\circ}$ C after H<sub>2</sub> gas absorption were different from reference samples. The characteristic elements including C, O, Na, Mg, Al, Si, Zr, K, Ni and Cu were detected by SEM-EDX in a nano-sized metal multilayer composite sample that generated the anomalous heat. The sample was fabricated with Cu and Ni layers in 96 nm thickness. Also, the depth profile of the sample with 96 nm layers of Cu and Ni indicated non uniform distribution for each element and it did not remain the layer composition. On the other hand, nano-sized metal multilayer composites formed by Cu and Ni with CaO or Y<sub>2</sub>O<sub>3</sub> indicated different surface state. However, the behaviour of Ca or Y derived from CaO or Y<sub>2</sub>O<sub>3</sub> containing Cu and Ni multilayer by the depth profile using TOF-SIMS was similar to the behaviour near the surface; they did not depend on each element. We guessed that any elements diffused through the similar process and interaction.

**Key Words**: Excess heat, H<sub>2</sub> gas, Nano-sized metal multilayer composite, SEM-EDX, TOF-SIMS

## 1. Introduction

 $D_2$  gas permeation through a nano-structured multilayer thin film composition of Pd, CaO and Pd substrate with a target element caused nuclear transmutation reactions [1-4]. Mitsubishi Heavy Industries observed permeation-induced nuclear transmutation reactions for the first time. These reactions were successfully replicated by such as Toyota R&D center [5]. In particular, transmutation reactions of Cs produce Pr. It might be considered that 2, 4 or 6 deuterons make fusion with the target materials and deuterium diffusion through nano-structured multilayer thin film was one of key factors. On the other hand, it has been reported that anomalous excess heat was observed using some metal composite under absorption of H<sub>2</sub> gas [6, 7]. Through what we have studied based on above factors and methods, heat bursts and excess energy generation occurred by using nano-sized metal multilayer composites on Ni substrate and H<sub>2</sub> gas. However, the reaction mechanism and the conditions to cause these phenomena has not been clarified. To obtain the key factors for understanding what is happening in a nano-sized metal multilayer composite, we have been investigating on elemental composition using various analysis methods.

# 2. Experimental

We used a Ni plate (25 mm square and 0.1 mm thickness, purity up to 99.9%, Furuuchi Chemical Co.) as the experimental sample. Surface of the multilayer thin films on a Ni substrate, prepared by Ar ion beam sputtering method, was used as the nano-sized metal composite.

Two nano-sized metal multilayer composites were placed in the center of the chamber, made of stainless steel (type 304) [8, 9]. The multilayer samples could be heated up by a ceramic heater (MS-1000R; Sakaguchi E. H Voc Corp.) in which a thermocouple (PtPtRh13%) was embedded. Heater temperature was measured by the thermocouple. Heater input power was supplied by a DC power source with constant voltage mode. The input voltage and current were measured both by voltage and current monitors provided by the power supply and independent voltmeter and amperemeter, respectively. Multilayer samples absorbed H<sub>2</sub> gas were conducted to heat up to 500~900°C for experiment. Each experimental sample has been contained in sample case.

SEM (Scanning Electron Microscope) observation for confirmation of the surface states of samples and EDX (Energy Dispersive X-ray spectroscopy) for elemental analysis were carried out using JSM-6500F (JEOL). Furthermore, two-dimensional elemental distributions and depth profiles by TOF-SIMS (Time of Flight Secondary Ion Mass Spectrometry) were performed using SIMS 5 (ION-TOF GmbH). Analysis sample was cut about 1/8 sections (6 x 12 mm) from experimental samples (25 mm square) in clean booth. Measurement area of TOF-SIMS was designated about 2 x 2 mm square from the film composition center.

# 3. Results and Discussion

#### 3.1. Excess heat generation and its evaluation

Nano-sized metal multilayer composites were constructed of Cu 2 nm and Ni 14 nm on Ni plate (25 x 25 x 0.1 mm, purity up to 99.9%, Furuuchi Chemical Co.). 2 nm thick CaO or  $Y_2O_3$  thin films were inserted into the Ni layers in some cases.

Figure 1 shows the structures of Ni based nano-sized metal multilayer composite which generated excess heat. The structures for the experimental samples were 3 layers of Cu 2 nm and Ni 14 nm (sample 1), 6 layers of Cu 2 nm and Ni 14 nm (sample 2) and Cu 2 nm and Ni 14 nm with CaO or  $Y_2O_3$  2 nm (sample 3, 4), respectively. The temperature dependence on the excess heat power of these four samples is shown in Figure 2.



**Figure 1.** Structures of nano-sized metal multilayer composite samples; 3 layers of Cu 2 nm and Ni 14 nm (**Sample 1**), 6 layers of Cu 2 nm and Ni 14 nm (**Sample 2**), 6 layers of CaO 2 nm, Cu 2 nm and Ni 14 nm (**Sample 3**), 6 layers of Y<sub>2</sub>O<sub>3</sub> 2 nm, Cu 2 nm and Ni 14 nm (**Sample 4**).



Figure 2. Temperature dependence on excess heat power for four samples.

Excess heat tended to increase with the temperature increase in sample  $1\sim3$ . However, sample 4 which containing Y<sub>2</sub>O<sub>3</sub> took a peak around 750°C. Released excess energy per H for the four samples indicated in Table 1. Sample 2, fabricated with Cu and Ni layers in 96 nm thickness, had highest total excess energy with 1.1 MJ. In addition, the released excess energy per H for four samples are too large to be explained by any known chemical reactions. We guessed that some condensed matter nuclear reactions were induced, however the reaction mechanism and the conditions to cause these phenomena have not been elucidated. We would like to search for difference of elemental composition or film structure and what is happening in the nano-sized metal multilayer composite. It is suggested that the material analysis is useful to obtain key factors to control condensed matter nuclear reactions.

**Table 1.** Released excess energy per H for four samples.

	3CuNi ( <b>1</b> )	6CuNi ( <b>2</b> )	CaO (3)	Y <sub>2</sub> O <sub>3</sub> ( <b>4</b> )
Absorbed H [mol]	7.6E-04	7.3E-04	5.1E-04	3.7E-04
Absorbed Number of H	4.6E+20	4.4E+20	3.0E+20	2.3E+20
Excess Energy per H [J/H-mol]	6.0E+08	1.5E+09	1.2E+09	6.8E+08
Excess Energy per H [eV/H]	6.3E+03	1.6E+04	1.2E+04	7.1E+03
Total Excess Energy [J]	4.6E+05	1.1E+06	5.9E+05	2.6E+05

# **3.2.** Analysis of nano-sized metal multilayer composite by SEM-EDX and TOF-SIMS

To identify what kind of reactions occurred by the interaction of the nano-sized metal multilayer composite with H<sub>2</sub> gas, we analysed about the surface states, depth profiles and mass spectra for before- and after-experiment samples using scanning electron microscope (SEM)/energy dispersive X-ray spectroscopy (EDX) and time of flight secondary ion mass spectrometry (TOF-SIMS).

Firstly, we observed the surface state and performed the elemental analysis of Ni plate sample as a blank run by SEM-EDX (JSM-6500F, JEOL) to compare the difference between before- and after-experiments (Figure 3). As seen in SEM image, grain aggregate is considered to have various sizes and forms. From the result of elemental analysis at point 1 by EDX, Ni peak derived from Ni substrate was detected and other elements were not found.

Next, sample 2 which was fabricated with 6 layers of Cu 2 nm and Ni 14 nm before and after experiments were analysed. Ni and Cu from the multilayer film and Ni substrate were detected. Furthermore, W was found a trace from before the experiment. We guessed that the cause of W contamination was from a filament of ion beam sputtering device. After heat generation experiment sample was observed to have unusual material on surface. Ni, Cu and W were detected similarly in the before-experiment sample on point 2, however, the characteristic elements including Ni, Cu, C, O, Na, Mg, Al, Si, Zr and K were found on point 3 (Figure 4). Although C and O are reasonable contamination, the origins of other elements are difficult to identify.



Figure 3. SEM image and EDX spectrum of Ni plate for blank run.



**Figure 4.** SEM image and EDX spectra of the sample 2 with 6 layers of Cu 2 nm and Ni 14 nm; (a) SEM image, (b) EDX spectrum of point 2, (c) EDX spectrum of point 3.

Figure 5 shows the results of depth direction analysis by TOF-SIMS (SIMS5, ION-TOF GmbH). The field of view was 101.6 x 101.6  $\mu$ m<sup>2</sup>. Cu and Ni of multilayer film composition distributed extensively, however the other elements were observed non uniform distribution. Although we considered that Mn and Fe were derived from stainless steel, the reasonable explanation why these elements were inverse distribution had not been cleared. From the results of the depth profile of sample 2, multilayer film composition formed by Cu and Ni did not remain. Na and K distributed near the surface, in contrast that, Al, Si and Mn were detected around interface.

Sample 1 with 3 layers of Cu 2 nm and Ni 14 nm, which had lower excess heat generation comparing sample 2, were performed to observe the surface state and to analyse the elemental composition using SEM-EDX. We did not find the same material with sample 2. According to the depth profile by TOF-SIMS, diffused film composition with Cu and Ni was seen and this result was in similar tendency with that of 6 layers and 3 layers of Cu and Ni samples (Figure 6).



**Figure 5.** Elemental distribution and depth profiles of sample 2 by TOF-SIMS; (a) sample size and analysis point (about 2 x 2 mm point from the filmed center), (b) measuring area (green square), (c) integrated elemental distributions of depth direction, (d) depth profiles.



Figure 6. Depth profiles of sample 1 by TOF-SIMS.

Subsequently, we performed to analyse the sample 3 of 6 layers of Cu 2 nm and Ni 14 nm with CaO. As seen in Figure 7, characteristic substance was found and O, Ca, Cu, Ni, Cr and Fe were detected on point 4 by EDX analysis. On the other hands, the sample 4 of 6 layers of Cu 2 nm and Ni 14 nm with Y<sub>2</sub>O<sub>3</sub> was observed with a number of holes on surface. Elemental analysis of point 5 detected O, Ni, Y and W derived from multilayers film composition. Elemental distribution in measuring area of the sample 4 looks ununiform in comparison with sample 3 as shown in Figure 8 (a). Cu, Ni, Y and Fe were largely distributed at right side in measurement area. We are now assuming that the un-uniformity of elemental distribution for two-dimensional and depth direction was caused by the elemental diffusion depending on the distribution of heat generation.

In addition, both of sample 3 and 4, multilayers film composition did not remain from the results of depth profiles. The behaviour of Ca or Y derived from CaO or  $Y_2O_3$ containing Cu and Ni multilayer was similar to that near the surface; intensities of Ca and Y were larger near the surface. Also, the distribution of Fe for each sample was resembling to Ni depth profile. By comparison the depth profile between sample 1 with 3 layers of Cu and Ni or sample 2 with 6 layers of Cu and Ni and sample 3 or 4 with CaO or  $Y_2O_3$ containing Cu and Ni, distribution of each sample was of different trend in the presence of the oxide (Figure 8).



**Figure 7.** SEM images and EDX spectra of sample 3 with 6 layers of Cu and Ni with CaO and sample 4 with 6 layers of Cu and Ni with Y<sub>2</sub>O<sub>3</sub>; (a) SEM image of sample 3, (b) EDX spectrum on point 4 of sample 3, (c) SEM image of sample 4, (d) EDX spectrum on point 5 of sample 4.



**Figure 8.** Elemental distributions and depth profiles of sample 3 with 6 layers of Cu and Ni with CaO and sample 4 with 6 layers of Cu and Ni with  $Y_2O_3$  by TOF-SIMS; (a) elemental distributions of sample 3 (top) and 4 (bottom), (b) depth profiles of sample 3 (left) and 4 (right).

## 4. Conclusions

SEM and TOF-SIMS analyses were performed for the nano-sized Cu/Ni metal multilayer composite and Cu/Ni metal with third material, CaO or Y<sub>2</sub>O<sub>3</sub>, composite that gave observation of anomalous excess energy generation. The surface states of each sample, Cu/Ni multilayer composites and Cu/Ni with CaO or Y<sub>2</sub>O<sub>3</sub> metal composites, were different by SEM observation. Cr, Mn and Fe detected by SEM-EDX and TOF-SIMS were derived from stainless steel during sputtering process. However, the reason is unclear why the surface distributions for Fe and Mn inversed on the sample 2 with 6 layers of Cu 2 nm and Ni 14 nm. In addition, the behaviour of Ca or Y derived from CaO or Y<sub>2</sub>O<sub>3</sub> containing Cu and Ni multilayer by the depth profile using TOF-SIMS was similar to that near the surface. We will continue to investigate further by various analysis methods paying attention to the discrimination of contaminations, and to elucidate the mechanisms of the anomalous heat generation phenomena.

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# Excess Energy Generation Experiments using a Nano-sized Multilayer Metal Composite and Hydrogen Gas

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### Abstract

The NEDO project [1] showed that anomalous heat, it was reported that heat generations far beyond 10eV/H or D were observed during NEDO project many times and reproduced. It was obtained by heating nano-sized particles, such as CuNiZr-O<sub>X</sub> or PdNiZr-O<sub>X</sub>, up to 200~300°C with D<sub>2</sub> or H<sub>2</sub> gas. On the other hand, transmutation reaction of Cs into Pr induced by D<sub>2</sub> gas permeation through nano-sized Pd and CaO multilayer composite was reported [2]. Based on these papers, we developed a new type of excess heat experiments using a nano-sized metal multilayer composite and hydrogen gas. Nano-size multilayer thin film samples consist of Ni and Cu were placed in the chamber. After evacuation of the chamber, samples were baked and cooled down. Next, H<sub>2</sub> gas was introduced into the chamber up to about 230 Pa at  $250^{\circ}$ C with a heater. Then, multilayer thin films started to absorb H<sub>2</sub> gas. After about 14h, H<sub>2</sub> gas was evacuated and simultaneously the samples were heated up by the ceramic heater up to 500~900°C. Anomalous heat generation was observed by the process of heating up samples. The excess heat was evaluated by the thermocouple embedded in the ceramic heater. Up to now, maximum released excess energy reached 1.1MJ and average released energy per absorbed total hydrogen was 16 keV/H or 1.5 GJ/Hmol. It cannot be explained by any known chemical process. It was suggested to be the consequence of the Condensed Matter Nuclear Reactions. We have carried out pre-experiments for heat assessment taking account of heat radiation from multilayer thin films using a radiation thermometer. As a result, heat burst phenomena were simultaneously detected by a radiation thermometer and the thermocouple in the ceramic heater. It shows that heat measurement using the thermocouple correctly reflects the surface temperature detected by the radiation thermometer. We are planning to evaluate excess heat by combing the thermocouple with the radiation thermometer.

Key Words: Excess heat, Anomalous heat, Hydrogen gas, Nano-sized metal, multilayer composite, Heat burst

#### 1. Introduction

Permeation-induced transmutation phenomenon, which is completely different from conventional transmutation by nuclear reactors or accelerators, was first reported in 2002 [2]. D<sub>2</sub> gas permeation through a nano-structured multilayer thin film composed of Pd and CaO thin film and Pd substrate with a target element induces nuclear transmutation reactions [3]-[6]. The temperature of the Pd complex is typically 70°C and the pressure of D<sub>2</sub> gas is 1 atm. Permeation-induced nuclear transmutation reactions were firstly observed at Mitsubishi Heavy Industries and were successfully replicated by other institutes such as Toyota R&D center [7]. Typical target element is Cs and produced element is Pr. Transmutation reactions of Sr, Ba, W into Mo, Sm, Pt were also observed by this method. It seemed that 2, 4 or 6 deuterons make fusion with the target materials. In this research, deuterium diffusion through nano-sized multilayer thin film was a key factor and the elemental analysis was important technique.

The Collaborative Research Project between six Japanese organizations funded by NEDO (New Energy and Industrial Technology Development Organization) on anomalous heat effects was done from Oct. 2015 to Oct. 2017 using Ni, Pd, Cu, Zr nano particles. Anomalous heat generation, which is too much to be explained by any known chemical process, was observed. Qualitative reproducibility was confirmed between the Kobe University and Tohoku University [8]-[11]. The authors replicated the experiments using nano Pd/Ni fabricated by glow discharge with D<sub>2</sub> gas developed by Dr. Mizuno [11]. In these experiments, nano-sized particles and diffusion of hydrogen and deuterium were one of key factors to observe the heat effects and precise heat estimation was crucial.

Combining factors and methods in nano-sized multilayer thin films by permeation experiments and anomalous heat generation experiments by NEDO projects, we developed a new type of excess heat experiments using a nano-sized metal multilayer composite and hydrogen gas. Larger excess energy per H was obtained using the present method [13].

#### 2. Experimental

A schematic of the experimental set-up is shown in Fig. 1(a). Two nano-sized metal multilayer composites were placed in the center of the chamber. The chamber, made of stainless steel (type 304), had two ports for introducing and evacuating gas, respectively. H<sub>2</sub> gas pressure was monitored by a Pirani gauge. The chamber could be evacuated by a turbo molecular pimp. The multilayer samples could be heated up by a ceramic heater (MS-1000R; Sakaguchi E. H Voc Corp.) in which a thermocouple (Pt-PtRh13%) was embedded. Heater temperature was measured by the thermocouple. The surface temperature of a sample was evaluated by an infrared radiation thermometer (IR-CAQ3CS; Chino Corp.). The detector was made of InGaAs and two wavelengths, 1.55µm and 1.35 µm, were used in this work. Gamma-rays were monitored by a NaI (Tl) scintillation counter (TCS-1172; Hitachi, ltd.) during all experiments, for safety. Heater input power was supplied by a DC power source with constant voltage mode. The input voltage and current were measured both by voltage and current monitors provided by the power supply and an independent voltmeter and amperemeter, respectively.



Figure 1. Experimental Set-up; (a) Schematic of Experimental Apparatus, (b) Detail Drawing around Nano-sized Multilayer Metal Composite.

A detailed drawing of the Ni based nano-sized metal multilayer composite is shown in Fig.1(b). It was composed of a Ni Plate (25 mm square and 0.1 mm thickness) and Cu-Ni multilayer thin film (25mm diameter circle and few 10nm thickness). Two nano-sized metal multilayer composite samples were heated with the ceramic heater (25 mm square and 2.2 mm thickness) through SiO<sub>2</sub> plates (0.3 mm thickness). If certain energy generation reactions would happen on the surface of samples, the temperature of the embedded thermocouple (heater temperature) would rise. Simultaneously, infrared emission detected by the radiation thermometer, which corresponds to surface temperature of the sample, would increase. Photos of the experimental set-ups and STEM image of Cu-Ni multilayer thin film are shown in Fig.2.



# Figure 2. Photos of Experimental Apparatus and Cross-sectional View of Nano-sized Metal Multilayer Composites; (a) Outer View of the Present Experimental Set-ups, (b) STEM (Scanning transmission electron microscope) Image of Cu-Ni Multilayer Thin Film.

A Ni plate (25 mm square and 0.1 mm thickness, purity up to 99.9%, Furuuchi Chemical Co.) was washed with acetone and annealed in vacuum ( $<10^{-4}$ Pa) at 900°C for 72 h. It was then cooled to room temperature in a furnace and washed with HNO/H<sub>2</sub>O to remove impurities on the surface of the Ni plate. The surface of the plate was covered by layers of Cu (2 nm) and Ni (14 nm) which were obtained by alternatingly sputtering 2 nm thick Cu and 14 nm thick Ni layers. 2nm thick CaO or Y<sub>2</sub>O<sub>3</sub> thin films were inserted into the Ni layers in some cases. The thicknesses of the layers were measured by a crystal thickness monitor. Fabrication process is performed by Ar ion beam sputtering. The samples are sputtered at room temperature and the voltage and current of the Ar beam are 1 kV and 10 mA, respectively.

The experimental procedure is as follows. Two nano-sized metal multilayer composites were placed in the chamber and baked for 1-2 days at temperature more than 200°C to remove H<sub>2</sub>O on the surface. After baking, H<sub>2</sub> gas was introduced into the chamber up to about 230 Pa at 250°C. Usually H<sub>2</sub> gas was loaded for about 16 hours. Then, H<sub>2</sub> gas was evacuate by the turbo molecular pump and simultaneously the samples were heated up by the ceramic heater up to 500~900°C. These process triggers heat generation reactions and observed excess heat. Typically, after 8 hours, the heater input was turned down and the samples were made cool down to 250°C. These processes (H<sub>2</sub> loading, heating up and cooling down samples) were repeated several times changing heating temperature.

During the above experimental procedure, hydrogen atoms are supposed to diffuse from the Ni plate through the nano-sized metal multilayer to the surface. The diffusion mechanism of hydrogen atoms is well known as "quantum diffusion" [14]. Hydrogen atoms are hopping from a site to another site in metal. We assume that hydrogen flux is one of the key factors to induce condensed matter nuclear reactions and the hydrogen flux is intentionally arranged by the present experimental method. Hydrogen flux J from the nano-sized metal multilayer composite to the chamber is caused by gradient of hydrogen concentration and gradient of temperature as shown in eq.1 [15].

$$\boldsymbol{J} = -nD(\nabla c + \frac{cQ^*\nabla T}{k_B T^2}) \tag{1}$$

where n is the number of lattice atoms per unit volume, c is hydrogen concentration defined as the hydrogen/host-metal atom ratio, D is diffusion coefficient and Q\* is the heat of transport.

# 3. Results and Discussion

#### **3.1.Excess Heat Estimation**

Heat analysis of this system is based on the following equation (2) as explained in Fig.3(a).

$$k\frac{T_{H}-T_{w}}{L}A_{H} + 2A_{S}\varepsilon\sigma(T_{S}^{4} - T_{w}^{4}) = P_{in} + H_{ex},$$
(2)

where k is thermal conductivity,  $T_H$  is the heater temperature,  $T_S$  is the surface temperature,  $T_W$  is wall temperature of the chamber, L is the length between the heater and wall,  $A_S$  is surface area of the sample,  $\varepsilon$  is the emissivity of the sample,  $\sigma$  is the Stefan–Boltzmann constant,  $P_{in}$  is the electrical heater input and  $H_{ex}$  is excess power that is generated heat power by the condensed matter nuclear reactions. This equation is obtained under the following assumptions.

- 1) Thermal conduction via H<sub>2</sub> gas is negligible as H<sub>2</sub> pressure is low enough.
- 2) Radiation from chamber wall is negligible because Tw is room temperature.
- 3) The electrical input power is constant. blank run, in which same sized Ni bulk.



Figure 3. Excess Heat Evaluation; (a) Model of Excess Heat Evaluation, (b) Relationship between Input Power(W) and Heater Temperature for Blank Run.

A blank run, in which same sized Ni bulk samples without multilayer thin films were used, was performed with the same procedure described above. Figure 3(b) shows the relationship between input power given to the ceramic heater and heater temperature detected by the thermocouple. Generated excess heat power can be evaluated based on the blank run result. Generated heat can be evaluated by the equation (1).

The radiation thermometer was introduced recently, so we now have many experimental results with the heater temperature only. As a first step of data analysis, experimental data analysis was done based on the assumption that  $\varepsilon$  is constant for Ni based nano-sized metal multilayer composite and Ni bulk. In the next step, excess heat will be evaluated more preciously by measuring  $\varepsilon$  for each sample.

#### **3.2.Excess Heat Generation and its Evaluation**

The structures for the samples were shown in Fig. 4. The ratio of Ni and Cu was the same for the four samples; Cu/Ni=1/7 in these examples. It was selected based on the past NEDO project results [1], [8]-[11]. And CaO and Y<sub>2</sub>O<sub>3</sub> were selected based on the



#### permeation-induced transmutation results [2]-[6].



Figure 5 shows pressure of the chamber and excess heat for each sample, and the temperature in the graph means heater temperature at each input. Red and blue lines mean excess heat and pressure of the chamber, respectively. At the beginning of each experiment, hydrogen gas was introduced to the chamber and absorbed into the Ni based nano-sized multilayer metal composite at 250°C. The pressure for each experiment gradually decreased as shown in the Fig.5. The amount of hydrogen absorbed by each sample was estimated based on the pressure change and temperature the chamber. After about 16 hours, H<sub>2</sub> gas was evacuated and simultaneously each sample was heated up by the ceramic heater. After that, excess heat more than input power was observed for each experiment as shown in Fig.5. The input power for each experiment, which were repeated in the order of about 19W, 9W and 27W, was stable during a one cycle; for example, 19W was applied to the ceramic heater from about  $6 \times 10^4$  sec to about  $9 \times 10^4$  sec in the Fig.5(a).

Comparing experiment (a), (b), (c) and (d), excess heat for experiment (b) was largest. Although input power for the first excess heat event (from  $6 \times 10^4$  sec to  $9 \times 10^4$  sec) in Fig. 5(a) and Fig. 5(b) was the same, heater temperatures were about 850°C and 880°C, respectively. A significant temperature difference was observed between the two cases.

For each experiment (c) and (d), which CaO and  $Y_2O_3$  was inserted to each Ni film, excess heat was different. Although input power for the third excess heat event (CaO: from  $2.3 \times 10^6$  sec to  $2.6 \times 10^6$  sec,  $Y_2O_3$ : from  $2.6 \times 10^6$  sec to  $2.9 \times 10^6$  sec) in Fig. 5(c) and Fig. 5(d) was the same, heater temperatures were about 910°C and 895°C, respectively. A significant temperature difference was also observed between the experiment (c) and (d). And the time dependence of excess heat for the four experiments was different; excess heat tended to increase decrease for the 6 Cu and Ni-layer experiment (b), however, excess heat decreased for the other experiments. Note that excess heat power and its time dependence changed depending on the structure the multilayer thin film region.



Figure 5. Examples on Excess Heat Generation; (a) Example #1: 3 Layers of Cu 2nm and Ni 14nm, (b) Example #2: 6 Layers of Cu 2nm and Ni 14nm, (c) Example #3: 6 Layers of CaO 2nm, Cu 2nm and Ni 14nm, (d) Example #4: 6 Layers of Y<sub>2</sub>O<sub>3</sub> 2nm, Cu 2nm and Ni 14nm.



Figure 6. Temperature Dependence on Excess Power for 4 Examples.

Figure 6 illustrates the temperature dependence on the excess heat power for the four examples. Excess heat tended to increase as temperature increase, however,  $Y_2O_3$  sample (Example #4) take a peak around 750°C. Temperature dependencies for the four samples looks like convex shapes. They did not depend on 4<sup>th</sup> power of temperature and it suggests that these observed excess heat powers were not attributed to the artifacts caused by thermal radiation.

	#1 (3 layers of Cu-Ni)	#2 (6 Layers of Cu-Ni)	#3 (6 Layers of CaO-Cu- Ni)	#4 (6 Layers of Y <sub>2</sub> O <sub>3</sub> -Cu-Ni)
Absorbed H [mol]	7.6E-04	7.3E-04	5.1E-04	3.7E-04
Absorbed Number of H	4.6E+20	4.4E+20	3.0E+20	2.3E+20
Total Excess Energy [J]	4.6E+05	1.1E+06	5.9E+05	2.6E+05
Excess Energy per H [J/H-mol]	6.0E+08	1.5E+09	1.2E+09	6.8E+08
Excess Energy per H [eV/H]	6.3E+03	1.6E+04	1.2E+04	7.1E+03

 Table 1.
 Released Excess Energy per Hydrogen for the 4 Examples.

Released excess energies per hydrogen for the four examples were evaluated based on the experimental results. Table 1 summarizes the amount of absorbed hydrogen, total excess energy and excess energy per absorbed hydrogen. The amount of excess energy was calculated by the time integration of excess powers for each experiment. They ranged from 0.26 MJ to 1.1 MJ. Although it seems highly unlikely that all the absorbed

hydrogen atoms reacted, we can still estimate that average released energies per absorbed total hydrogen for example #1, #2, #3 and #4 were 6.3 keV/H, 16 keV/H, 12 keV/H and 7.1 keV/H, respectively. Obviously, the released excess energy per hydrogen atom for all the experiments demonstrated here are too large to be explained by any known chemical reactions. This strongly suggests that some condensed matter nuclear reactions were induced in our experiments, although it is not clear at present what kind of reactions occurred. According to the results, about  $10^{-3}$  of the absorbed hydrogen might react if the condensed matter nuclear reactions would release energy order from 1MeV to 10MeV. Identification of reaction products is very important future work, in addition to more preciously excess heat evaluation.

#### 3.3. Surface Temperature Detected by a Radiation Thermometer

Heat burst phenomena were observed by the radiation thermometer and the thermocouple in the heater simultaneously as shown in Fig.7. Output from the radiation thermometer, which corresponds to the surface temperature of samples, is plotted as the upper blue line, and heater temperature is plotted as the lower red line in the upper graph of Fig.7. Input electrical power and room temperature around the chamber are drawn in the lower graph. A significant simultaneous increase of surface and heater temperature were observed twice, while no significant changes for input electrical power and room temperature were detected during these burst events. This means that heat measurement by the thermocouple embedded in the ceramic heater correctly reflected surface temperature detected by the radiation thermometer.



Figure 7. Simultaneously Detected by a Radiation Thermometer Looking at the Surface of the Multilayer Thin Film and a Thermocouple Located in the Center of Heater.

#### 4. Concluding Remarks

New type of excess heat experiments using a nano-sized metal multilayer composite and hydrogen gas. Anomalous excess energy generation was observed by using nano-sized metal Cu/Ni multilayer composite and Cu/Ni metal with third material (CaO, Y<sub>2</sub>O<sub>3</sub>) composite. Maximum released excess energy reached 1.1MJ and average released energy per absorbed total hydrogen was 16 keV/H or 1.5 GJ/H-mol (6 Layers of Cu/Ni multilayers composite). It cannot be explained by any known chemical process. It was suggested that it was the consequence of the Condensed Matter Nuclear Reactions. Even though used nano-sized order very thin films composite (about 100nm), the significant difference of excess energy and behaviour of heat was observed. we are planning to evaluate excess heat by combing the thermocouple with the radiation thermometer.

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# A theoretical study on the possible change of the phonon dispersion relation due to the nuclear reaction in two-dimensional lattice II

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#### Abstract

It is well known that phonon dispersion relations of crystalline solids sensitively depend on the lattice structures. So, lattice defects or impurities change phonon dispersion relations from those of pure crystals. As we know, nuclear reactions in solids change the sizes of impurities and the number of impurities. This means that we can detect the nuclear reaction in solids by observing the states of phonon. In our previous works, we showed the possibility of the change of phonon dispersion relations due to the nuclear reactions in solids by using one-dimensional and two-dimensional theoretical models. For example, we consider the following reaction. When some impurity ions get closer through the lattice gaps, they collide with some probability and the nuclear reactions occur. After that, the structures of the crystal will change and it makes shifts of phonon dispersion relations. If they are uniform reactions in macroscopic lattice, they can be easily detected. However, it is not easy for the local reactions. In this study, we show the method how to detect the local changes of lattice defects due to the nuclear reactions by observing the local phonon modes.

(keywords; phonon dispersion relation, local phonon mode, nuclear reaction in solids)

#### 1 Introduction

In JCF19, we described the possibility that the phonon dispersion relation changes under the influence of the nuclear reactions in the solids by using two-dimensional models [1]. That study assumed the uniform reactions in the lattice. An example is showed again in Fig.1.



Fig. 1. An example of DD reactions in two-dimensional lattice, where 1/2 deuterons migrate and all deuterons happen to react. (Fig.7 of ref[1])

In the left-hand side of the figure, the deuterons uniformly stored in the two-dimensional lattice are drawn and the migration through the gaps of the lattice are shown by the purple arrows. In the right-hand side of the figure, He atoms and vacant stable sites created by the nuclear fusions are shown. In both sides of the figure, the primitive cells are shown by the thick lines. For the case of this reaction by uniformly arranged interstitial deuterons, examples of the possible changes in the phonon dispersion reaction were given in the previous paper [1].

The reactions by the uniformly arranged impurities are easy to deal with. However, they are not realistic. In this study, the local mode of phonon dispersion relations induced by the local nuclear reactions are discussed [2].

#### 2 Monoatomic one-dimensional lattice

At the bigining, a brief explanation is given for the phonon dispersion relation of a monoatomic one-dimensional lattice, which is illustrated in Fig.2.



Fig. 2. A monoatomic one-dimensional lattice, whose mass of an ion, force constant between neighboring two ion and lattice constant are M, a and C, respectively.

When we use the nearest neighbor approximation, the equation of motion of an ion in a monoatomic one-dimensional lattice can be written as

$$M\frac{d^2u_n}{dt^2} = C(u_{n+1} + u_{n-1} - 2u_n) , \qquad (1)$$

where M and C mean mass of an ion and the lattice constant, respectively. As the first step, only longitudinal oscillations are considered and transverse oscillations are omitted. Therefore, the solution  $u_n$  is a longitudinal displacement of the *n*-th ion from the equilibrium position along the lattice line whose lattice constant is a. An oscillatory solution of the equation of motion that satisfies Bloch's theorem can be written as

$$u_n = U e^{ikna} e^{-i\omega t}$$
  $(n = \cdots, -1, 0, 1, \cdots)$ , (2)

where characters U, k and  $\omega$  mean the amplitude, wave number and the angular frequency, respectively. In order to make Eq.(2) satisfy Eq.(1), the relation between

the angular frequency and the wave number should satisfy

$$\omega = \sqrt{\frac{4C}{M}} \left| \sin\left(\frac{qa}{2}\right) \right| \ . \tag{3}$$

This is called phonon dispersion relation of longitudinal acoustic (LA) mode. This expression shows a repetition of the region of  $-\frac{\pi}{a} < k < \frac{\pi}{a}$ , which is called the first Brillouin zone. At the zone boundary,  $\omega$  takes the maximum value  $\omega_{max} = \sqrt{\frac{4C}{M}}$ .

# 3 Effect of a substitutional light impurity in the monoatomic one-dimensional lattice

We explain here how the phonon dispersion relation is affected if an ion in the pure lattice shown in Fig.2 is replaced by a light impurity ion. This effect is introduced in many papers and books, for example Kittel's book as the localized mode in phonon dispersion. The sketch of this lattice is shown in Fig.3.



Fig. 3. A one-dimensional lattice including a substitutional light impurity at the origin, where m and M mean mass of light impurity and host ion, respectively. The relationship between m and M is represented by m < M.

Strictly speaking, the equilibrium distance between ions should be different depending on the position, and so is the force constant, however we regard them as constants. In this model, the equation of motion of n-th ion is written as

$$M_n \frac{d^2 u_n}{dt^2} = C(u_{n+1} + u_{n-1} - 2u_n) , \qquad (4)$$

where  $M_n$  and  $u_n$  mean the mass and the displacement of the *n*-th ion, respectively. As the light ion exists at the origin,  $M_0 = m$  and  $M_n = M$  for  $n \neq 0$ .

A possible solution of Eq.(4) is written as

$$u_n = U e^{ikna} e^{-i\omega t} e^{-|n|\alpha} \qquad (n = \cdots, -1, 0, 1, \cdots) ,$$
 (5)

where the factor  $e^{-|n|\alpha}$  in Eq.(5) works as the damping factor for the effect of the light impurity at the origin. This is proved as follows. The equations of motions for

n = 0 and 1 are written as

$$m\frac{d^2u_0}{dt^2} = C(u_1 + u_{-1} - 2u_0) \tag{6}$$

$$M\frac{d^2u_1}{dt^2} = C(u_2 + u_0 - 2u_1) .$$
(7)

Here, only one pair of n = 0 and 1 is taken up, but also the same results as described below are obtained for n = 0 and any integer but zero. Therefore, generality is not lost even if only one case is handled. If we consider the solution for the zone boundary  $k = \pm \pi/a$ , then it is written as

$$u_n = U(-1)^n e^{-i\omega t} e^{-|n|\alpha} , (8)$$

where the factor  $(-1)^n$  emerged from the Bloch factor  $e^{ikna}$  in Eq.(5) at zone boundary. Substituting Eq.(8) into Eq.(6) and Eq.(7), we obtain

$$\omega^2 = \frac{2C}{m} \left( 1 + e^{-\alpha} \right) \tag{9}$$

$$\omega^2 = \frac{C}{M} \left( 2 + e^{-\alpha} + e^{\alpha} \right) . \tag{10}$$

Considering that these two equations are consistent with each other, we obtain a quadratic equation for  $e^{\alpha}$ , and the solution is given by

$$e^{\alpha} = \frac{2M}{m} - 1 . \tag{11}$$

Therefore, the damping constant  $\alpha$  is written as

$$\alpha = \log\left(\frac{2M}{m} - 1\right) \ . \tag{12}$$

This means that constant  $\alpha$  is always real and positive because M > m, and  $e^{-|n|a}$  in Eq.(5) works as damping factor. Furthermore, the angular frequency  $\omega$  is redefined by substituting Eq.(11) into Eq.(9) or Eq.(10) as

$$\omega = \omega_{max} \sqrt{\frac{M^2}{2mM - m^2}} . \tag{13}$$

This means that angular frequency of the local mode at zone boundary is larger than that of the pure acoustic mode, because  $0 < 2mM - m^2 < M^2$ .

Except for the zone boundaries, an imaginary component of  $\omega$  occurs. In this case, the solution  $u_n$  vanishes or diverges over time. Therefore, both of them should not be considered. Thus, the local mode appears as a point on the zone boundary.



Fig. 4. Phonon dispersion relation of monoatomic one-dimensional lattice (solid line) and a local mode (circle filled in red) caused by a substitutional light impurity included in a pure lattice.

This is shown in Fig.4 with LA mode of pure lattice.

There are some possibilities to detect nuclear reactions by using this effect. If the mass m of the light impurity changes by nuclear reaction, the value of  $\omega$  in Eq.(13) will also change. For the case of DD reaction in Pd lattice, the mass number of the impurity will change from 2 to 4. Substituting M = 106 and m = 2 into Eq.(13),  $\omega/\omega_{max} = 5.2$  is obtained. However, if m changes from 2 to 4,  $\omega/\omega_{max}$  changes to 3.7. This is an oversimplified one-dimensional calculation, but it is estimated that the change from 5.2 to 3.7 can be detected in actual measurements.

#### 4 Application to the two-dimensional space

The previous sections showed a one-dimensional case. However, the path of the two nucleons approaching through the lattice line of one-dimensional lattice is difficult to understand and the reaction is not realistic. In this section, the theory for the local mode is expanded into two-dimensional space.

Considering a substitutional light impurity exists at the origin of the two-dimensional simple cubic lattice with lattice constant a, the solution like Eq.(5) is estimated to be

$$\mathbf{u}_{pq} = \mathbf{U}e^{i\mathbf{k}\cdot\mathbf{R}_{pq}}e^{-i\omega t}e^{-|\mathbf{R}_{pq}|\alpha/a} \quad (p,q=\cdots,-1,0,1,\cdots) , \qquad (14)$$

where vectors  $\mathbf{u}_{pq}$  and  $\mathbf{U}$  are included in the lattice plane. In Eq.(14),  $\mathbf{k}$  is a wave number vector, and  $\mathbf{R}_{pq}$  means lattice points defined by

$$\mathbf{R}_{pq} = a(p\hat{\mathbf{x}} + q\hat{\mathbf{y}}) , \qquad (15)$$

where  $\hat{\mathbf{x}}$  and  $\hat{\mathbf{y}}$  are unit vectors that are orthogonal to each other. A sketch of a two-

dimensional simple cubic lattice with a substitutional light impurity at the origin is shown in Fig.5.



Fig. 5. A two-dimensional simple cubic lattice including a substitutional light impurity at the origin, where m and M mean mass of a light impurity and host ion, respectively.

In the nearest neighbor approximation, the total potential energy of this system is written as

$$V = \frac{C}{2} \sum_{pq} \left[ (x_{p+1,q} - x_{pq})^2 + (y_{p+1,q} - y_{pq})^2 + (x_{p,q+1} - x_{pq})^2 + (y_{p,q+1} - y_{pq})^2 + (x_{p-1,q} - x_{pq})^2 + (y_{p-1,q} - y_{pq})^2 + (x_{p,q-1} - x_{pq})^2 + (y_{p,q-1} - y_{pq})^2 \right], \quad (16)$$

where  $x_{pq}$  and  $y_{pq}$  are components of displacement vector  $\mathbf{u}_{pq}$ . Though  $C_{pqp'q'}$  dependent on (p,q) and (p',q') should be used for the exact calculation, we used C within the nearest neighbor approximation. Calculating the partial derivative of V with respect to the component  $x_{pq}$ , the equation of motion for  $\hat{\mathbf{x}}$  direction is obtained as

$$M_{pq}\frac{d^2x_{pq}}{dt^2} = C(-4x_{pq} + x_{p+1,q} + x_{p,q+1} + x_{p-1,q} + x_{p,q-1}) .$$
(17)

This equation describes a motion of ion (p,q) surrounded by the four ions (p + 1,q), (p,q+1), (p-1,q) and (p,q-1). The similar equation can be obtained for  $\hat{\mathbf{y}}$  direction.

The Phonon dispersion relation can be considered for the case of the lattice illustrated in Fig.5 by using Eq.(14) and Eq.(17). If we assume the wave number vector to be  $\mathbf{k} = k\hat{\mathbf{x}}$ , then Bloch factor in Eq.(14) becomes  $e^{-ikpa}$ . Substituting this solution
into Eq.(17), we obtain

$$-\omega^{2} M_{pq} e^{-\sqrt{p^{2}+q^{2}\alpha}} = k \left( -4e^{-\sqrt{p^{2}+q^{2}\alpha}} + e^{ika} e^{-\sqrt{(p+1)^{2}+q^{2}\alpha}} + e^{-\sqrt{p^{2}+(q+1)^{2}\alpha}} + e^{-ika} e^{-\sqrt{(p-1)^{2}+q^{2}\alpha}} + e^{-\sqrt{p^{2}+(q-1)^{2}\alpha}} \right) .$$
(18)

This gives

$$\omega^{2} = -\frac{k}{m} \left( -4 + e^{ika}e^{-\alpha} + e^{-\alpha} + e^{-ika}e^{-\alpha} + e^{-\alpha} \right)$$
(19)

and

$$\omega^{2} = -\frac{k}{M} \left( -4 + e^{ika} e^{-\alpha} + e^{(-\sqrt{2}+1)\alpha} + e^{-ika} e^{\alpha} + e^{(-\sqrt{2}+1)\alpha} \right) , \qquad (20)$$

where  $m = M_{00}$  and  $M = M_{10}$ . In order to find  $\alpha$  so that Eq.(19) and Eq.(20) are consistent to each other, we should solve

$$\frac{1}{m}\left(-2 + \cos(ka)e^{-\alpha} + e^{-\alpha}\right) = \frac{1}{M}\left(-2 + \cosh(ika - \alpha) + e^{(-\sqrt{2}+1)\alpha}\right) .$$
(21)

At the zone boundary  $k = \pi/a$ , this equation becomes

$$-\frac{2}{m} = \frac{1}{M} \left( -2 - \cosh \alpha + e^{(-\sqrt{2}+1)\alpha} \right) .$$
 (22)

And furthermore, this is rewritten as

$$\cosh \alpha = e^{(-\sqrt{2}+1)\alpha} + 2M\left(\frac{1}{m} - \frac{1}{M}\right)$$
(23)

The existence of a positive real solution for this equation can be known by the shape of the both sides of Eq.(23) as a function of  $\alpha$ . Seeing Fig.6, we can understand that Eq.(23) has a positive solution when  $2M\left(\frac{1}{m}-\frac{1}{M}\right)$  takes a positive value. At this point,  $\alpha$  works as a damping constant in Eq.(14) and it is a local mode of twodimensional cubic lattice including a substitutional light impurity. Except for the zone boundary,  $\alpha$  has an imaginary component as in the one-dimensional case. In this case,  $\omega$  also has an imaginary component and the solution in Eq.(14) will banish or diverge.

For the cases of other directions of wave propagation, similar disucssion is available. And three-dimensional lattice can be applied for explaining the local mode of phonon dispersion. We will study them in near future.



Fig. 6. Solution for the damping factor  $\alpha$  by using Eq.(23). The intersection of the two functions is the solution. In this calculation, we assume the constant part of the right-hand side to be 1.0.

#### 5 Conclusions

In this study, the changes of phonon dispersion relations due to the local nuclear reactions in solids was shown by using the limited simple models. It was found that the local mode exists not only in one-dimensional but also in two-dimensional lattice as a spot at the zone boundary. When the nuclear reaction in the solid occurs, the phonon dispersion relation also changes for the reason shown in this study. If this is detected, it can be said that a nuclear reaction has been detected.

In near future, we will study the local mode induced by a substitutional impurity in fcc Pd, This will give a new method how to detect nuclear reaction in Pd.

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## Calibration of Sendai mass-flow-calorimeter and heat

# measurement of recycled sample

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#### [Abstract]

We have attempted to improve the calorimetry based on the flow calorimeter for better accuracy of the excess heat measurement in the metal-hydrogen gas system. In addition to the measurement of the heat flow transferred to the oil fluid, which has been performed so far, heat flows due to the conduction heat of the material connecting the reaction chamber and the outside are measured as well as those transmitted through vacuum (i.e., thermal radiation and energy transfer by molecules). All these are added to the measured heat flow value. The effect of adding the radiant heat flow is significant: the heat-measurement efficiency has improved to be 90% or more from 70%, and the uncertainty of the deduced total heat flow has been reduced from 0.84 W to 0.39 W, about 50% smaller. Further, variations in measurement efficiency originated from dis- and re-assembly of the experimental device are evaluated to be within  $\pm$  0.89%. Applying this calorimetric method, we have re-examined excess heat for the sample PNZS4 (Pd0<sub>.044</sub>Ni<sub>0.31</sub> Zi<sub>0.65</sub>) which showed anomalous excess heat in the previous experiment. The excess power of 2.24  $\pm$  1.39 W was observed over a long period of time when the heater input was 150W.

#### 1. Introduction

The mass-flow-calorimeter developed by the Kobe University—Technova group [1] has enabled accurate heat flow measurement in excess-heat generation experiments in the composite metal nanoparticle-hydrogen (deuterium) gas system up to a temperature of about 300 °C by using oil coolant. In the NEDO project [2], experiments using same samples and similar equipment were conducted at two locations in Kobe and Sendai, and demonstrated the reproducibility of the anomalous excess heat generation phenomenon. [3-6]

The calorimetric system we used in the NEDO project was designed and manufactured based on the mass-flow-calorimeter originally designed by Takahashi and Kitamura.[1] In this system, a cooling pipe through which a heat transfer fluid flows is attached to an outer wall of a reaction chamber, and a heat flow from the reaction chamber is measured from a temperature rise of the cooling oil fluid. Therefore, the advantage is that the temperature rise basically is independent on the thermal properties of the sample inside the reaction chamber, since the heat exchange is not performed directly with the sample, but with the chamber. However, it is almost impossible to compare the results with and without the sample under exactly the same condition because the sample exchange necessarily involves the dis- and re-assembly of the vacuum and reaction chambers. Moreover, the measured heat flow cannot be all of the generated heat, due to heat loss by other paths than removed by the fluid.

The ratio of the amount of measured heat flow to that of actually generated is called the heat-measurement efficiency (called heat recovery rate in [1,3-6]), which is not a constant but depends on the amount of generated heat in such a way that the larger the heat, the larger the loss. In previous experiments, the heat-measurement efficiency is about 70% at the minimum. It is considered that most of the loss is due to heat radiation from the outer wall of the reaction chamber. The excess heat power is about 2 to 10 W for the input power of around 130 W in previous experiments [3-6]. In such a situation where the excess power is a few % of the input power (and the measured error is  $\pm 1.5\%$  of output power [4]), bringing the heat-measurement efficiency close to 100% by adding heat flow through other paths than the fluid would increases the reliability of measured values of the anomalous heat generation. In particular, when the heat flow measured by the other path has a correlation with that of the oil fluid, it can be expected that the uncertainty of each measurement is compensated with the other, and the accuracy of the total summed value is improved.

In the present work, aiming to increase the heat-measurement efficiency to more than 90% we have attempted to improve the calorimetry by adding heat flows that are not measured previously; those removed through the gas inlet tube and cables, and radiated from the reaction chamber. In addition, the uncertainty of the deduced excess heat is evaluated based on a strict discussion on the calibration of the heat-measurement efficiency. Moreover, we have performed excess heat measurement with the sample used in the NEDO experiment to apply the present method.

#### 2. Calorimeter setup

A schematic diagram of our flow calorimeter is shown in Fig. 1. Since our device is based on the one already reported by Kitamura et al. [1,4,5] and also reported by Iwamura et al. [3,6], the important and different points are briefly described here.

The reaction chamber with a volume of 500 cm<sup>3</sup> and the vacuum chamber in which the reaction chamber is suspended are the essential part of the device. The experimental

sample is contained in the reaction chamber and hydrogen/deuterium gas is supplied from the gas inlet pipe suspending the reaction chamber.



Fig. 1. Schematic view of essential part of calorimeter.

The inside of the reaction camber can be heated up by an electric heater installed on the center of the chamber (W1) and another wounded around the wall (W2). The heat flow generated in the chamber (including the one from the heaters) passes through an oil pipe helically surrounding the outer wall of the reaction chamber, and is carried away by the fluid flowing from bottom to top in the oil pipe. The flow rate is measured by a flow meter. The vacuum chamber is evacuated by a dry pump, and most of the generated heat flow from the reaction chamber is converted into an increase in the temperature of the fluid flowing through the oil pipe. In order to keep the thermal environment of the reaction chamber as constant as possible, the outer wall of the vacuum chamber is kept at constant temperature with a water stream through a spirally wrapped pipe.

Temperatures at various points are measured by thermocouples (TC) and resistance temperature detectors (RTD). The major points where the temperatures are measured are indicated in Fig. 2. The most important are those at the bottom of the chamber (TC IN) and at the top of the chamber (TC OUT). Many other sensors including about 20 TCs are set at various locations to evaluate the conduction heat flow from the chamber as well as to confirm normal operation during the experiment: a pressure gauge for gas pressure in the vessel, a vacuum gauge for the vacuum chamber and a flow meter for oil flow measurement are shown in Fig. 1.



Fig. 2. Temperature measured points.

The major difference from the original setup at Kobe University [1] is that the ceramicfiber covering case that filled the gap between the outer wall of the reaction chamber and the inner wall of the vacuum chamber is removed. In the present work, the heat flow due to the radiation is calculated by temperature measurement and added to the measured value, instead of reducing the heat radiation loss with the insulation. For this purpose, the outer wall of the reaction chamber is covered with Al foil, and additional TCs are placed to measure temperatures at the points 0 cm (TC H1), 8.5 cm (TC H2), 15 cm (TC H3) and 20 cm (TC H4) from the bottom of the reaction chamber. Furthermore, to increase the heat flow measured by the circulating oil even slightly, the position of TC OUT is brought closer to the top of the vessel by about 5 cm.

The experimental conditions are almost the same as those in [3,6]: the oil Barrel Therm 400 (BT400) is used for the cooling oil, which is cooled after circulation and adjusted so that TC IN becomes about 25 °C. Usually, measurements are performed when the flow rate of BT400 is about 14.5 cm<sup>3</sup>/min., the gas pressure in the reaction chamber is between 0.4 and 0.6 MPa, and the pressure in the vacuum chamber is between 0.3 and 0.6 Pa. The data logger MX110-UNV-M10 made by Yokogawa Electric was used for collecting data. Measured signals are digitized and recorded every second for later off-line analysis.

## 3. Heat flow to measure

The present heat measurements are based on data of the steady state where the chamber temperature is constant after changing the input power of the heater in the reactor chamber.

Under these conditions, the heat flow generated in the reaction chamber is equal to that flowing out of the chamber. We have examined to capture the heat flow out of the chamber as completely as possible, specifically, 90% or more.

The most major part is the heat transferred to the fluid oil, which is the thermal energy of the oil acquired during the circulation around the reaction vessel. Thus, the transferred heat Q<sub>oil</sub> can be described as

$$Q_{oil} = f \int_{T_{in}}^{T_{out}} c(T') \ \rho(T') \ dT' \quad , \tag{1}$$

where f is the volume flow rate [cm<sup>3</sup>/min], c (T) is the specific heat [J/g K] and  $\rho$ (T) the mass density [g/cm<sup>3</sup>] of the oil, and T<sub>in</sub> and T<sub>out</sub> are the temperatures of the oil before and after the circulation. In the calculation of eq. (1), both  $\rho$ (T) and c(T) are considered up to the first order term of T as,

$$\rho(T) = \rho_0 + \rho_1 T \quad ; \rho_0 = 1.06, \rho_1 = -6.93 \times 10^{-4}, \quad (2)$$
  

$$c(T) = c_0 + c_1 T \quad ; c_0 = 1.50, c_1 = 3.40 \times 10^{-3}. \quad (3)$$

Then, Qoil is given as

$$Q_{oil} = f \Delta T \left( \rho(T_{av}) \ c(T_{av}) + \frac{\rho_1 \ c_1}{12} \ \Delta T^2 \right) \quad , \qquad (4)$$

where  $\Delta T = T_{out} - T_{in}$  and  $T_{av} = (T_{in} + T_{out})/2$ .

In addition, heat flows to the outside due to heat conduction between the reaction and the vacuum chambers, although the amount is expected to be very small. The total amount of the heat conduction  $Q_{cond}$  is the sum of each contribution, such as the gas pipe supporting the reaction chamber, thin electric wires of the temperature sensors, electric wires of the heaters and the oil pipe itself, and, thus, described as

$$Q_{cond} = \sum_{i} \lambda_i \ \frac{S_i \ \Delta T_i}{d_i} \quad , \qquad (5)$$

Here,  $\lambda_i$  is the thermal conductivity [W/m K] of each heat transfer medium,  $S_i$  is the crosssectional area [m<sup>2</sup>] perpendicular to the heat flow, and  $d_i$  is the distance [m] between two points at which temperature is measured, and  $\Delta T_i$  is the temperature difference [K] between the two points.

Moreover, there are measurable heat flows transmitted in a vacuum: the heat radiation  $(Q_{rad})$  and the heat propagation by dilute free molecules  $(Q_{fmh})$  in a vacuum.  $Q_{rad}$  is approximately evaluated by dividing the reaction chamber surface into 4 parts (with the vacuum chamber into 3 parts) and summing the heat radiation of each surface  $(Q_i)$  as

$$Q_{rad} = \sum_{i=1}^{4} Q_i = \sum_{i=1}^{4} S_i \varepsilon_i \left( \sigma T_{b,i}^4 - \sum_{j=1}^{7} F_{i,j} J_j \right) \quad . \tag{6}$$

Here, i = 1 to 4 correspond to the 4 parts of the reaction chamber surface,  $S_i$  is the surface area,  $\varepsilon_i$  is the emissivity,  $\sigma$  is the Stefan-Boltzmann coefficient, and  $T_{b,i}$  is the surface

temperature. The last term of eq. (6) corresponds to the radiation coming into the i-th surface from all the divided surfaces (j = 5 to 7 are 3 parts of the inner surface of the vacuum chamber),  $F_{i,j}$  represents the radiation shape factor, and radiosity  $J_j$  is the solution of the simultaneous equations [7] (see Appendix).

 $Q_{fmh}$  can be calculated from the pressure P and the temperature difference  $\Delta T$  between the vessel surface and the vacuum chamber, by  $Q_{fmh} = aP\Delta T$ . The parameter *a* was experimentally determined by measurements at different vacuum pressures.

All of the above-mentioned heat flows are measured and summed up as

 $Q_{\text{meas}} = Q_{\text{oil}} + Q_{\text{cond}} + Q_{\text{rad}} + Q_{\text{fmh}}.$  (7)

However,  $Q_{\text{meas}}$  is always smaller than the generated power  $Q_{\text{gene}}$  due to unmeasurable convection heat of  $D_2$  gas and underestimation of  $Q_{\text{rad}}$ . Therefore, we define the heat-measurement efficiency  $\eta$  as

$$Q_{\text{meas}} = \eta Q_{\text{gene}} = \eta \left( Q_{\text{heat}} + Q_{\text{ex}} \right), \qquad (8)$$

where  $Q_{heat}$  is the heat flow generated by the heaters (W1 and W2) and  $Q_{ex}$  is the excess power generated in the reaction, if occurred. Once  $\eta$  is known, one can deduce  $Q_{ex}$  from  $Q_{meas}$  by  $Q_{ex} = Q_{meas}/\eta - Q_{heat}$ . As to determine  $\eta$  as a function of  $Q_{meas}$ ,  $Q_{meas}$  is measured for the input  $Q_{heat}$  under the condition of  $Q_{ex} = 0$  (we call this blank or background (BG) run). We determine 3 parameters *a*, *b* and *c* by approximating the relation to

 $Q_{\text{heat}} = aQ_{\text{meas}} + bQ_{\text{meas}}^2 + cQ_{\text{meas}}^3, \qquad (9)$ and obtain  $\eta$  (Q<sub>meas</sub>) as

 $\eta = 1/(a + bQ_{\text{meas}} + cQ_{\text{meas}}^2).$ (10)

#### 4. Experimental Procedure

The procedure is similar to those reported in [3,6]. In the BG run, 1300 g of zirconia ZrO<sub>2</sub> beads which is thought not to generate heat are packed in the reaction vessel, while in the foreground (FG) run 100 g of PNZ4S sample which was used in [4] with 1200 g of zirconia ZrO<sub>2</sub> beads are used.

In the experiment, first, a sample is set in the reaction chamber, and it is installed in the vacuum chamber, which is, then, evacuated. Before admitting D<sub>2</sub> gas into the reaction chamber, the chamber is evacuated until the pressure drops to about  $10^{-5}$  Pa, and then the heater is turned on for a vacuum bake-out. After about 50-hour baking out, the heater is turned off. When the reaction chamber has cooled down to the room temperature, D<sub>2</sub> gas is filled in the chamber until the gas pressure reaches  $(3\sim7)\times10^5$  Pa.

In the BG run, data were accumulated under the following conditions in order to determine the heat-measurement efficiency  $\eta$ : heater input power Q<sub>heat</sub> form 60 to 165 W, oil flow rate f from 13.5 to 15.5 cm<sup>3</sup>/min, and vacuum chamber pressure P<sub>ic</sub> from 0.2 to

0.7 Pa. The measurement of one run was continued for 48 hours in taking into account the time required for the system to be steady state (several hours). In the foreground run, PNZS4 samples were measured in the same way as the BG run. The measurements were performed for  $Q_{heat} = 60, 90, 130$  W, but f was fixed at 14.5 cm<sup>3</sup>/min, and P<sub>ic</sub> was about 0.3 Pa.

## 5. Results and discussion

Fig. 3 shows several temperature data at the newly added points to derive  $Q_{rad}$  and  $Q_{fmh}$ . The horizontal axis shows the vertical height based on the thermocouple H2, and the vertical axis shows the temperature. The red, blue, and black points represent the temperature of each thermocouple on the reaction chamber surface when the heater power is 150 W, 120 W, and 90 W, respectively. The temperature increases with an increase in  $Q_{heat}$  at any points. The temperatures at the side of the vacuum chamber, F1, F2 and F3 in Fig. 2, are about 25°C regardless of  $Q_{heat}$ .



Fig. 3. Temperature of surface of the reaction chamber.

The temperature at the side surface covered by the heater (W2) increases with a very small slope as the height increases. Since the heater covers from 5 to 28 cm, the temperature at H2 is much lower than the temperature extrapolated from the slope between H3 and H5. In contrast, the temperature at E1 on the upper surface is higher than the extrapolated one. In order to deduce the value of  $Q_{rad}$ , a straight line connecting points on the side surface is employed for the temperature distribution, and the emissivity of the Al cover is assumed to be 0.1.

Fig. 4 shows each component of the heat flow deduced from the temperature measurement. The black circle is  $Q_{oil}$  (plotted at 1/4 times value), the square is  $Q_{rad}$ , the

triangle is  $Q_{cond}$ , and the diamond is  $Q_{fmh}$ . Contributions from  $Q_{cond}$  and  $Q_{fmh}$  are very small, about 2% of  $Q_{meas}$ , while  $Q_{rad}$  is the second largest after  $Q_{oil}$ , reaching up to 12%. They increases almost linearly with  $Q_{heat}$ , although, on closer inspection, the increase in  $Q_{rad}$  is slightly larger than the linear one.



Fig. 4. Each component of heat flow as a function of Qheat.



Fig. 5. Heat-measurement efficiency  $\eta$  vs.  $Q_{meas}$ .

Fig. 5 shows the results for the heat-flow-measurement efficiency  $\eta$  defined by eq. (8), as a function of  $Q_{meas}$ . The red circles are the data for all Qs ( $Q_{meas} = Q_{oil} + Q_{rad} + Q_{cond} + Q_{fmh}$ ) that include all the heat flow measurements newly added in the present work, while the blue circles for  $Q_{oil}$  alone, i.e., employed in the previous experiments.  $\eta(Q_{meas})$  in eq.

(10) that best reproduces the data is shown by the solid line, Values of  $\eta$  for all Qs become up to 90%, being about 10% higher than those for Q<sub>oil</sub> alone. Furthermore, the Q<sub>meas</sub> dependence of  $\eta$  has become almost constant; the difference in  $\eta$  in the measured range is only within 2% for all Qs while 5% for Q<sub>oil</sub> alone. This is due to the fact that Q<sub>rad</sub>, which is proportional to the fourth power of temperature, is added to the measured quantity of Q<sub>meas</sub>, although not perfect. The solid line in the figure is a curve fitted to reproduce the experimental value of  $\eta$ , and is used to determine the thermal power generated in the reaction vessel from the measured value of Q<sub>meas</sub> by eq. (8).



Fig. 6. Heat-measurement efficiency  $\eta$  vs oil flow rate f.

The effect of  $Q_{rad}$  added to  $Q_{meas}$  can be seen more directly in Fig. 6 showing the oil flow rate dependence of  $\eta$  measured with a large change in oil flow rate. The red circles are the data for all Qs and the blue ones for  $Q_{oil}$  alone. The value of  $\eta$  obtained for  $Q_{oil}$ alone is highly dependent on the oil flow rate, while that for all Qs is almost independent. The reason is as follows: As the flow rate increases, the amount of heat transferred to the oil increases, the reaction chamber is cooled, and the surface temperature of the chamber decreases. Therefore, the heat flow due to the heat radiation from the surface is reduced, and, then,  $Q_{oil} + Q_{rad}$  becomes almost constant. As a result, the uncertainty of  $\Delta \eta/\eta$  due to the variation in oil flow rate ( $\Delta f = \pm 0.1 \text{ cm}^3/\text{min}$ ) is reduced by an order of magnitude, from 0.2% (for  $Q_{oil}$  alone) to 0.02% (for all Qs).

In order to estimate the uncertainty of the value of  $Q_{ex}$  deduced by equation (8),  $Q_{ex}$  are plotted against  $Q_{meas}$  for the BG run in Fig. 7. The red circle corresponds to all Qs, and the blue square corresponds to  $Q_{oil}$  alone. As seen, values of deduced  $Q_{ex}$  are scattered around  $Q_{ex} = 0$ , and the spread is smaller for all Qs than for  $Q_{oil}$  alone. Since each point

is an averaged value based on the measurement over at least 24 hours for steady state, random errors of raw data of every 10 seconds are completely canceled out. Thus, this spreading is not due to random fluctuations of measured quantities and we consider that increasing the number of measurements and/or points does not reduce the width of spreading. One standard deviation ( $\sigma$ ) is calculated to be 0.13 W for all Qs and 0.28 W for Q<sub>oil</sub> alone and is shown by red and blue dotted lines in Fig.7. This indicates that the uncertainty of Q<sub>ex</sub> deduced through the calibration curve is improved by about 40% by employing the present method. We will apply the value of 3 $\sigma$  as the uncertainty of Q<sub>gene</sub> to increase the reliability of the result on the anomalous excess heat generation. Thus, when the measurement of all Qs is used, the uncertainty of Q<sub>ex</sub> is  $\pm$  0.39 W ( $\pm$  0.84 W for Q<sub>oil</sub> only). Here, we call this  $\Delta_1$ . This is the variation of Q<sub>meas</sub> deduced through a specific  $\eta$  curve.



Fig. 7. Qex plotted against Qmeas for BG run

In addition, there is a possibility that the  $\eta$  curve in a foreground (FG) run, for which the experimental devise is disassembled and reassembled, may be slightly different from the one determined in the BG run. This is a problem on the reproducibility of  $\eta$  curve due to device dis- and re-assembly. We have estimated the uncertainty originated from the reproducibility of  $\eta$  curve by using two datasets acquired before increasing the number of points for measuring the temperature for newly added Q<sub>rad</sub>. Fig. 8 shows a plot of  $\eta$  vs Q<sub>meas</sub> of two sets of data (red circles and blue squares). They were measured under the same conditions, but the work of dis- and re-assembling the vacuum and reaction chambers and exchanging the sample in the reaction chamber was performed after acquiring the first data set. One sees a slight difference that the red circles are systematically larger than the blue ones. There is a maximum difference of 0.35% between the two  $\eta$  curves (the red and blue dotted lines) that best fit each data. It is assumed that the difference in the  $\eta$  curve that occurs with every exchange work is within three times this range (i.e., 1.05%), and that the probability of taking any curve in between is evenly distributed. Then, the uncertainty of  $\eta$ , corresponding to 3 standard deviation, is evaluated to be  $\Delta \eta / \eta = \pm 0.91\%$ . The contribution of  $\Delta \eta / \eta$  to  $\Delta Q_{ex}$  (we call it  $\Delta_2$ ) is  $\Delta_2 = \pm (Q_{meas}/\eta) \times (\Delta \eta / \eta)$ , which is about  $\pm 0.9W$  at  $Q_{heat} = 100W$ : It should be noticed that  $\Delta_2$  is more than twice larger than  $\Delta_1$ .



Fig. 8. Plot of  $\eta$  vs Q<sub>meas</sub> of two sets of data of BG run.

In Fig. 9, we show a plot of  $Q_{ex}$  as a function of elapsed time of the FG run using the sample PNZS4 (Pd0.044Ni0.31 Zi0.65) and D2 gas. The figure shows the behavior after 850 hours when the baking-out is completed. Red dots are  $Q_{ex}$  values for every 10 seconds derived from the data collected at each time. The value of each point fluctuates between about ±1W, but this is mainly due to the minimum digit number of each sensor. As already discussed, since the fluctuation is considered random, the uncertainty of the time averaged  $Q_{ex}$  ( $\langle Q_{ex} \rangle$ ) becomes negligibly small for a long-time measurement like the present experiment. Blue circles are the values of  $\langle Q_{ex} \rangle$ , respectively, for  $Q_{heat} = 90$ , 120 and 150 W from the left to right. The horizontal bar represents the time interval for the measurement at each  $Q_{heat}$ , and the vertical bar shows the uncertainty of  $\langle Q_{ex} \rangle$ , derived as  $\Delta = (\Delta_1^2 + \Delta_2^2)^{1/2}$ , with  $\Delta_1$  and  $\Delta_2$  discussed in the previous two paragraphs.



Fig. 9. Plot of Qex as a function of elapsed time for the FG run.

A small peak is seen around 930 h when D<sub>2</sub> gas is introduced and Q<sub>heat</sub> is set to 90W: this is probably due to  $H_2$  gas absorption by Pd. Values of  $\langle Q_{ex} \rangle$  are deduced after the heat flow becomes steady at each Q<sub>heat</sub>. At Q<sub>heat</sub> = 90 W, <Q<sub>ex</sub>> is only 0.43 W, which is not exceeding the range of the uncertainty ( $\pm 0.91$  W). However, Q<sub>ex</sub> increases in response to an increase in  $Q_{heat}$ . The values of  $\langle Q_{ex} \rangle$  are 1.55 (±1.16) W at  $Q_{heat} = 120$  W and 2.24  $(\pm 1.42)$  W at Q<sub>heat</sub> = 150 W. The total generated energy for Q<sub>heat</sub> = 120 W during the period from 1600 to 1900 h is, then, 1.67 ( $\pm$ 1.25) MJ and that for  $Q_{heat} = 150$  W for 500 h is 4.03  $(\pm 2.56)$  MJ. The sample used in this measurement is the re-oxidized PNZ4S sample. The measured  $\langle Q_{ex} \rangle$  values is about 1/3 of those in the first use ( $\langle Q_{ex} \rangle \sim 3W$  at  $Q_{heat} = 80W$ and  $\langle Q_{ex} \rangle \sim 5.5W$  at  $Q_{heat} = 134W$ ) [3]. We have another experience of having used a reoxidized sample: the experiments have been performed on the CNZ5s (CuNiZr) sample with H<sub>2</sub> gas.[6] In this case, <Qex> of the reused sample was reduced by about half. Kitamura et al. also reported excess power reduction for a reused sample (PNZ3r) [1]. These examples suggest that it is difficult for a reused sample to completely recover the initial state with higher reaction rate. The present work, however, shows that the excess heat generation continued, albeit small, for a long time measurement.

#### 6. Conclusions

We have attempted to improve the calorimetry based on the calorimeter developed by Kobe University – Technova group, in order to obtain better reliability of the heat flow measurement in the anomalous excess heat measurement for the metal-hydrogen gas system. Two things were done: One is to improve the heat-measurement efficiency of the calorimeter. Another is to evaluate the uncertainty of the excess heat based on a strict discussion on the calibration of the efficiency curve.

First, in addition to the measurement of  $Q_{oil}$ , which is only measured in the previous measurements, other heat losses are measured independently: they are  $Q_{cond}$  which is due to the conduction heat of materials connecting the reaction chamber and the outside,  $Q_{fmh}$  which is the heat propagated by dilute free molecular in vacuum, and  $Q_{rad}$  due to the radiation transmitted through the vacuum. All these quantities, including  $Q_{oil}$ , were added to the measured heat flow  $Q_{meas}$ . The effect of adding  $Q_{rad}$  is significant, and the heat-measurement efficiency  $\eta$  which is about 70% without the radiation measurement has improved to 90% or more. Further, it was found that the uncertainty of  $Q_{meas}$  due to the deviation in the oil flow rate becomes negligibly small, because of the existence of the correlation between the oil flow rate and  $Q_{rad}$ ,

Second, for a long-time measurement the uncertainty of the averaged excess power is mainly two sources: the variation of  $Q_{meas}$  deduced through a specific  $\eta$  curve and the variation of  $\eta$  curve associated with dis- and re-assembly of the experimental device. We have evaluated each uncertainty with  $3\sigma$ , and obtained  $\Delta Q_{ex} = \pm 0.39$  W for the former and  $\Delta \eta/\eta = \pm 0.91\%$  for the latter. It should be noticed that the contribution of the latter is larger by two times or more.

Applying the improved calorimetric method, we have measured excess heat for the sample PNZS4 (Pd0.044Ni0.31 Zi0.65) which showed anomalous excess heat in the previous experiment. The excess power of  $2.24 \pm 1.42W$  was observed over 500 hours when the heater input was 150W. The sample used in this measurement is the re-oxidized PNZ4S sample, and the measured  $\langle Q_{ex} \rangle$  values is about 1/3 of those in the first use of the sample. It is suggested that there might be a difficulty for the reused sample to completely recover the initial state with higher reaction rate.

## Appendix. $J_i$ and $F_{i,j}$ in eq. (6) to evaluate $Q_{rad}$

The radiant heat emitted from the surface has two components: one is emitted by the surface itself depending on its temperature, and the other is reflection of the electromagnetic wave coming from various surfaces. To evaluate  $Q_{rad}$ , the outer surface of the reaction chamber and the inner surface of the vacuum chamber are divided into four and three parts, respectively, as shown in Fig. A-1. The radiosity (total radiation leaving a surface per unit time and per unit area)  $J_i$  [W/m<sup>2</sup>] emitted from the i-th part is expressed as follows,

$$J_i = \varepsilon_i E_{b,i} + (1 - \varepsilon_i) \sum_{j=1}^7 F_{i,j} J_j$$
. (A-1)

Here,  $E_{b,i}$  is radiation flux of black body,  $\sigma T_{b,i}^4$ , and  $F_{i,j}$  is radiation shape factor.[7] Eq. (A-1) is a set of seven simultaneous equations, and  $J_i$  of this solution is substituted into eq. (6) of the text. The calculated radiation shape factor  $F_{i,j}$  is shown in Table A-1.



Fig. A-1. Seven parts of the surface of the reaction and vacuum chamber.

i∖j	1	2	3	4	5	6	7
1	0.000.E+00	0.000.E+00	0.000.E+00	0.000.E+00	2.791.E-02	9.721.E-01	0.000.E+00
2	0.000.E+00	0.000.E+00	0.000.E+00	0.000.E+00	1.072.E-04	9.996.E-01	2.834.E-04
3	0.000.E+00	0.000.E+00	0.000.E+00	1.395.E-01	0.000.E+00	7.974.E-01	6.304.E-02
4	0.000.E+00	0.000.E+00	1.676.E-01	0.000.E+00	0.000.E+00	3.324.E-01	4.999.E-01
5	6.529.E-03	3.659.E-04	0.000.E+00	0.000.E+00	0.000.E+00	9.877.E-01	5.375.E-03
6	8.527.E-03	1.280.E-01	6.394.E-03	2.219.E-03	3.704.E-02	7.844.E-01	3.342.E-02
7	0.000.E+00	9.674.E-04	1.348.E-02	8.898.E-02	5.375.E-03	8.912.E-01	0.000.E+00

Table A-1. Calculated radiation shape factor for the geometry in Fig. A-1.

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