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ANOMALOUS HEAT FLOW AND ITS CORRELATION WITH DEUTERIUM FLUX IN A GAS-LOADING DEUTERIUM-PALLADIUM SYSTEM

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ABSTRACT

A special experimental device was designed to test the anomalous thermal effect of Pd with deuterium flux (D_f) caused by deuteron diffusion passing through a thin wall of a Pd tube under a D_2 pressure difference across the Pd wall. It is found that the variation of the flux was the significant precursor of the anomalous heat, because a remarkable heat flow was detected when the D_f was becoming obviously larger. The experiment was repeated for more than 16 times, and the maximum heat flow detected was 4.8mW whereas the accuracy of the calorimeter is better than 30 μW. There were no heat flow detected when the temperature of the device was increased and when the D_2 pressure difference equaled to zero. Neither heat flow nor flux was observed in the control experiment using N_2.gas. The results of TLD (Themoluminescence dosimeter) detection implied a nuclear origin of the heat flow because the dosage of radiation in reaction vessel was often higher than that in reference vessel.

1. INTRODUCTION

The anomalous nuclear phenomenon that observed in metal lattice containing deuterium has been studied for more than 13 years since 1989. But the nature of the phenomenon is still unclear. This experiment results in a gas-loading D/Pd system let us to assume that one of the most important conditions to induce the anomalous effect is the deuterium flux in solid. In addition the anomalous exothermic effect can be often observed in decreasing the temperature of the device other than in increasing it.

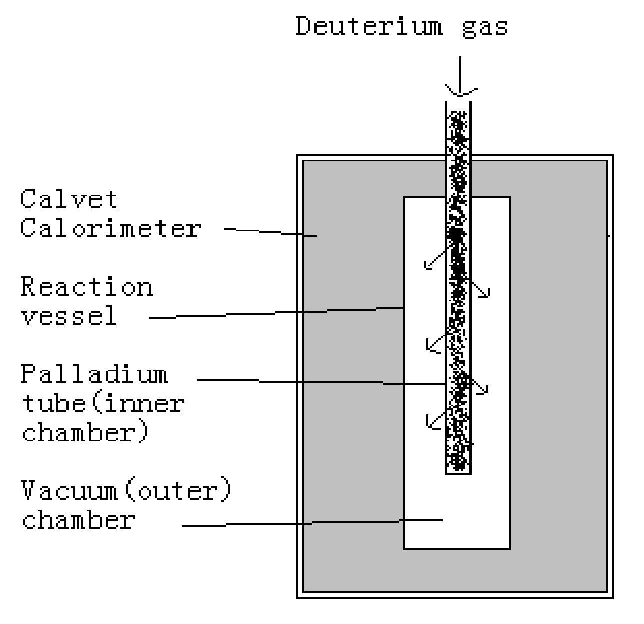

Fig. 1. Schematic of device for detecting the correlation between heat flow and deuterium flux

In 1994, M.Mckubre [1] of SRI proposed that the deuterium should be circulated and Y. Iwamura [2] of MHI studied the nuclear transmutation in the presence of D_2 flux in 1998. But the correlation between heat effect and deuterium flux has not been investigated so far. To meet this requirement we designed an experimental device (Fig. 1) in which a continuous flux could appear while the deuterium permeated through the thin wall of a Pd tube. When the flux was changing, the anomalous heat flow could be detected by a high precision Calvet calorimeter which detection limit is about 30 μW. Finally we used thermoluminescence dosimeter (TLD) to detect the 30keV~3MeV radiation in reaction vessel so as to count characteristically for the nature of the heat flow.

2. EXPERIMENTAL

2.1 Main materials and apparatus

Palladium (containing 20% Ag) tube was offered by Beijing Institute of Non-ferrous Metallurgy

Diameter: 4mm
Length: 26mm
Thickness: 0.1mm
Heat processing: degassing in situ at temperature of 270℃, 30 Pa for 3.5 hours before using.

Deuterium gas was supplied by the Ministry of Nuclear Industrial of China

Maximum pressure: 2 atms
Purity: 99.9%

Calorimeter was imported from Setaram Ltd. of France

Temperature range: ambient to 300℃
Calorimetric resolution: 0.12 μW
Detection limit in power: 2 to 5 μW
Time constant: 100 seconds

TLD was offered by Institute of Chemical Defense of China.

Size: ϕ4.5×0.8mm
Linear dose range: 10^{-7} to 12Gy
Energy dependence (photon: 30keV~3MeV): <20%

2.2 The set up of experimental system

2.2.1 *Reaction vessel and gas/vacuum systems*

Figure 2 shows the schematic of reaction vessel connected with gas supplier and vacuum systems. The Pd tube was sealed at lower end, and welded to a gas supply pipe at the upper end. Thus the Pd tube formed an inner chamber in the reaction vessel. The gas pressure inside that inner chamber was monitored by a pressure gauge. The volume between the Pd tube and the reaction vessel is the outer chamber. The gas pressure in the outer chamber was monitored by another gauge also. The reaction vessel made up of stainless steel is of 12.5 cm^3 in volume. All the connections in the system were hermetically sealed with Metal-Metal or Metal-PTFE-Metal method and passed the test by a helium leakage detector. The solder for welding is made of silver and copper.

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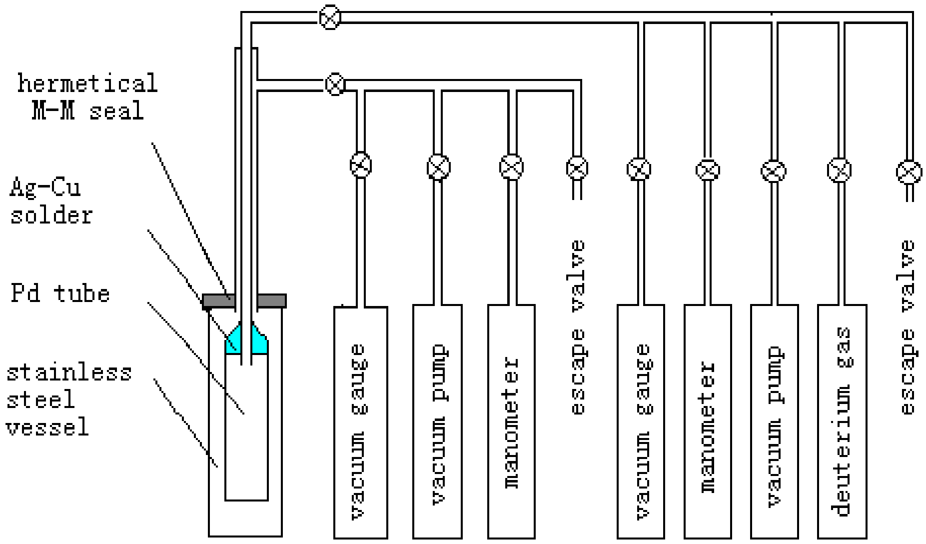

Fig. 2. The schematic of the D-Pd gas-loading system

2.2.2 *Calorimeter and recording/controlling systems*

Figure 3 gives the connection of calorimeter, data collecting and program controlling systems. In which both reaction (11) and reference (9) vessels are tightly encased into the holes on the cylinder (7) of the calorimeter. The difference of heat flow signal detected by two piles of thermocouples (8), which were counter-connected to each other, was sent into data-collector (5), signal amplifier (4) and a computer (1) for storage and processing. The programmed temperature controlling system consisted of a thermocouple (10), a heater wire (6), voltage comparator (3), a program generator (2) and also the same computer as above.

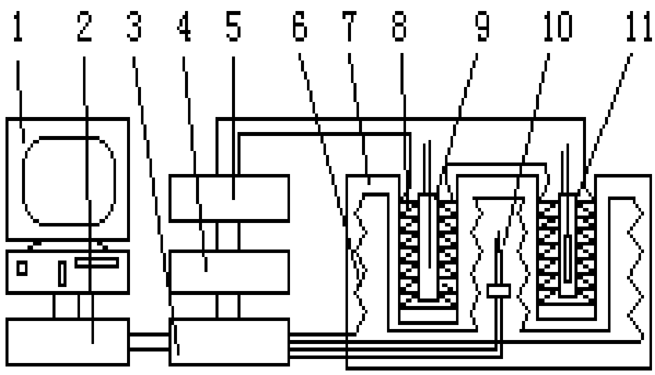

Fig. 3. The set up of the calorimeter and its recording/processing systems

Before the experiment we learnt the system properties by examining the noise and drift of heat flow of calorimeter at 35℃, 100℃, 150℃, 200℃, respectively. The accuracy of heat flow controlling within 3 hours was less than 30 μW. Besides we also did the calibration of the system by inputting an exact amount of energy into reaction vessel and then calculating the heat the calorimeter recorded. Based on these we confirmed that the system was very stable and reliable for the experiment. The relative error of calorimeter was about 1% if the heat production in the system was more than 4 Joules. Table 1 gives the test results of stability and calibration.

Table 1 The noise/drift of heat flow and calibration results of our D/Pd gas-loading system

Temperature (℃)	Heat flow(μ W)		Calibration results		
	noise	drift	E_{input} (J)	E_{record} (J)	error(%)
35	<1	<10	0.100	0.098	2
100	<1	⩽10	3.600	3.545	0.9
150	<1	<15	0.100	0.097	3
200	<1	<30	4.000	3.946	1.4

2.3 Experimental procedures

2.3.1 *Anomalous heat and system temperature*

Vacuum both chambers with rotary pumps (pumping speed is 2L/sec.) and heat the device up to 270℃ at the rate of 2℃/m. Keep the system at this temperature for 3.5 hours; then, turning off the heating power half an hour after filling deuterium gas (P_{D2} ~1.2atm) into the inner chamber. The system temperature was naturally decreasing from then on.

A significant heat flow started spontaneously as the system temperature was decreased near 134℃ (T_{onset}). The heat flow reached its maximum at 132.18℃(T_{max}). The exothermic process endured for 3 hours or so and ended at about 100℃. The same experiment cycle was repeated for 3 times and some similar heat flows were observed in all of the 3 experiments.

Afterwards the system was heated again up to 200℃ at 0.4℃/m, and cooled down naturally with the same pressure conditions as that in T_{max}=270℃. Anomalous heat flows were also detected in these repeated experiments.

In order to examine the behavior of our system when the temperature was increased, we heated it up to 270℃ at 0.4℃/m and 200℃ at 0.25℃/m, respectively, with exactly the same sequences as above. No obvious thermal effect was detected in the period of temperature rising

2.3.2 *Anomalous heat and system pressure*

We have run the experiment for 10 times using the same sequence as that in 2.3.1, but the deuterium pressure in the inner chamber of reaction vessel was different for each experiment. As the pressure difference ($\triangle P=P_{in}-P_{out}$) became smaller and smaller the heat flow was getting weaker and weaker too. The anomalous heat flows were usually appeared in all of experiments when the system was cooled down to near 130℃. When the $\triangle P=0$, no anomalous heat was detected. It was noticed that when the heat flow appeared the pressure of inner chamber dropped quickly. The changing rate of the pressure is faster than that in ordinary period by a factor of 4; and the pressure in the outer chamber suddenly went up although it was pumped continuously. This was a clear evidence that there should be a deuterium flux permeating through the wall of the Pd tube. We also noticed that as soon as the heat flow disappeared, the variation of the pressure in the inner chamber became slowly again. Finally we substituted deuterium gas with nitrogen gas as a control experiment, neither heat flow nor pressure variation was observed in the same period.

2.3.3 *Anomalous heat and TLD*

In order to study the nature of the heat flow. We tied 4 pieces of TLDs on the surface of Pd tube and put same amount of TLD into reference vessel to compare difference between two vessels. Two pieces of TLDs were monitoring the ambient background of the laboratory and five pieces for calibration. As the same sequence as in 2.3.1, we repeated the experiment for four times in which there was a control one of Nitrogen-Palladium system. The TLDs for calibration and detection were all sent to the Institute of Measurement Science (Chinese Academy of Science), who is domestically authorized in radiation detection.

3. RESULTS AND DISCUSSION

3.1 Heat, temperature behavior and SRT theory[3]

Table 2 shows that the heat flow appeared only when the temperature of the D/Pd system was decreasing. For the experiments No1 to No.3, the Pd tube was cooling down from 270^{o}C, and for experiment No.4 to No.6,. the Pd tube was cooling down from 200^{o}C. It shows that in all these six experiments, heat flow appeared. However, when the temperature was increasing from 35^{0}C to 270^{o}C in No.7 or to 270^{o}C in No.8, there was no heat flow. It might imply that a negative temperature gradient in the radial direction of Pd tube might be a condition for the anomalous effect. We may also see that the heat flow usually appeared in the temperature range of 120~140℃ despite that the system was cooling down from 270℃ or 200℃. An interesting point is that the duration of the exothermic effect is in the order of 10^4 seconds. This characteristic timing has appeared in various “anomalous phenomena” of D/Pd system all over the world.

Table 2 Dependence of the heat flow on the temperature trends of D/Pd system

Exper. No.	T_{onset} (℃)	T_{max} (℃)	Duration (sec)	Max.heat flow (mW)	△H (kJ/mol Pd)	Tempr. range (℃)	Tempr.rate variation (℃/m)
1	134.1	132.2	12454	4.82	3.12	270~35	-0.61~ -0.05
2	126.2	120.2	8720	0.85	1.78	270~35	-0.61~ -0.05
3	122.7	118.9	9307	1.50	1.59	270~35	-0.61~ -0.05
4	124.4	119.6	11070	2.26	2.03	200~35	-0.40~ -0.05
5	139.6	135.8	8084	2.01	1.48	200~35	-0.40~ -0.05
6	119.2	114.3	7368	1.10	1.02	200~35	-0.40~ -0.05
7	—	—	—	—	—	35~270	0.4
8	—	—	—	—	—	35~200	0.25

It is possible to understand this behavior based on the resonant tunneling theory.[3] If the heat flow is caused by the d+d fusion reactions in Pd; there must be a resonant tunneling effect to penetrate the Coulomb barrier between two positively charged deuterons. This is the resonance between the nuclear energy level and the energy level in the crystal lattice. The nuclear energy level is fixed by the nuclear force; however, the energy level in the crystal lattice is affected by the lattice constant. When the lattice constant increases with temperature, usually, the energy level in the crystal lattice will shift down; hence, the resonance between two energy levels might be destroyed by the resonance effect itself unless the heat of fusion reaction is taken away. When the Pd tube is cooling down, there must be a cooling mechanism to take away the heat from the system; then, it is possible to keep the resonance for a longer period than that when the Pd tube is heated up. That is why we could not observe any heat flow when the Pd tube was being heated up.

3.2 Heat, pressure difference and deuterium flux

Table 3 gives the experimental results of anomalous heat, and its dependence on pressure difference(△P) across the Pd tube based on 2.3.2. We can learn from it that as the pressure difference became smaller the heat flow was correspondingly reduced. The duration of exothermic effect became shorter also. And the peak position was moved towards the lower side of temperature. When the pressures between the inner and outer chambers became equal, the anomalous heat flow could no longer be detected.

Table 3 Anomalous heat and the dependence on pressure difference(△P) across the Pd tube

Experi-ment No.	Heat (Joule)	$△P_{max}$ (atm)	T_{onset} (℃)	T_{max} (℃)	Exothermic duration (sec)	Temperature decreasing rate (℃/m)
1	4.39	2.0	139.4	134.6	9850	-0.4~-0.1
2	3.54	1.5	144.3	139.6	11092	-0.4~-0.1
3	2.59	1.4	146.6	139.7	9837	-0.4~-0.1
4	2.38	1.3	140.7	132.8	9798	-0.4~-0.1
5	0.97	1.2	139.4	131.1	6594	-0.4~-0.1
6	0.89	1.1	137.1	127.8	6852	-0.4~-0.1
7	0.73	1.0	138.2	126.2	7296	-0.25
8	0.24	0.9	135.1	127.9	5210	-0.4~-0.1
9	—	0	—	—	—	-0.4~-0.1
10	—	0	—	—	—	-0.25

Usually, the diffusion coefficient of deuteron inside the palladium is supposed to be dependent on temperature. The lower the temperature is, the smaller the diffusion coefficient. Hence, it was expected to observe the diffusion flux through the thin wall of Pd tube would drop when the Pd tube was cooling down. However, a sudden increasing of deuteron flux was observed when the temperature of Pd tube was down to the range of 140°C~130°C as described before. This could not be explained by the diffusion process. It was an unusual permeation of deuterons. This .unusual permeation of deuterons had the feature of resonance (the lower curve in Fig.4), because it appeared only in a narrow interval of the temperature. The more important was that this resonant permeation of deuterons was correlated with an anomalous heat flow (the upper curve in Fig.4). This anomalous heat flow appeared just after the onset of the resonant permeation. The time constant of the Calvet calorimeter is supposed to be 100 seconds(empty vessel) to 250 seconds (full vessel). In our experiment, this anomalous heat flow appeared 140 seconds after the resonant permeation. Moreover, the diffusion coefficient was supposed to be independent of the trends of the temperature. No matter, the temperature of Pd is increasing or decreasing, the diffusion coefficient at the same temperature should be same, however, this sudden permeation of deuterons appeared only when the temperature of Pd tube was increasing; hence, we might assume that this resonant permeation would be the very phenomenon we were looking for, i.e. the selective resonant tunneling of Coulomb barrier.

Usually, when deuteron was absorbed by palladium, the enthalpy of formation of Pd deuteride is positive, i.e. there should be an exothermic effect when deuteron enters the thin wall of the Pd tube. Since we detected also a sudden rising of the pressure in the outer chamber, it implied a flux of deuterons which was desorbing from the outer surface of the Pd tube. It was an endothermic process. Hence, this endothermic process was accompanied by an exothermic process when a deuteron flux was penetrating the thin wall of Pd tube. This endothermic process might not be in balance with this exothermic process, but it is a slow diffusion process. Hence this resonant feature of heat flow could not be explained by the unbalance between the absorption and desorption.

In order to distinguish this slow diffusion process from the fast resonant permeation, we calculated the derivative of the pressure in the outer chamber, dP/dt. (Figure 4 lower curve). When dP/dt turned into positive suddenly, it meant a deuteron flux suddenly appeared.. dP/dt reached its maximum when this resonant permeation reached its maximum. dP/dt became smaller and then turned into negative, because the continuous pumping would pump out the deuterium gas until a new balance between pumping and diffusion flux was established later.

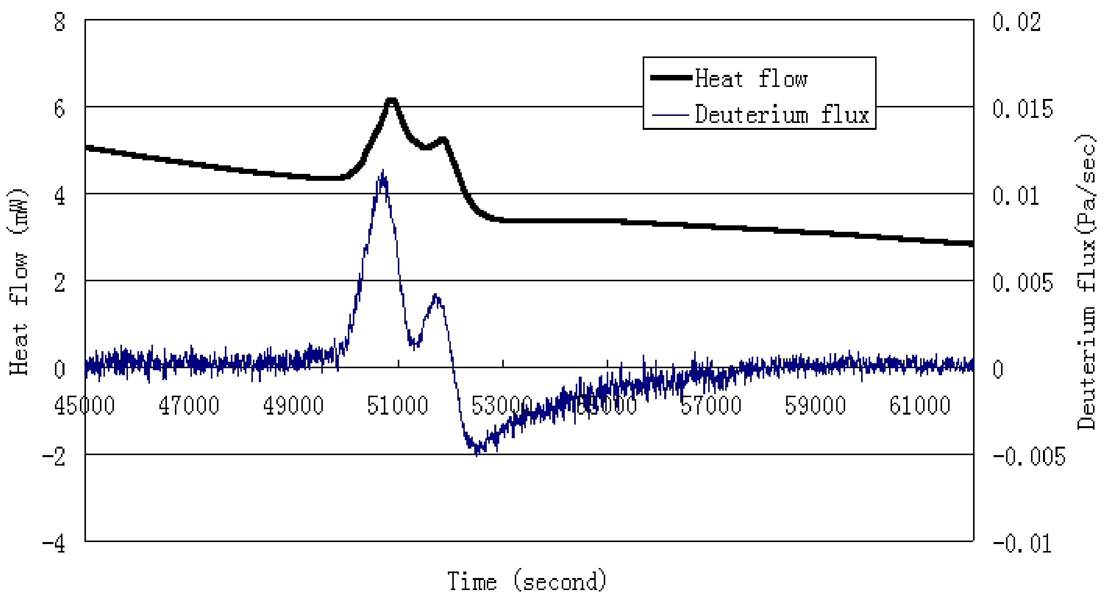

Fig. 4. Correlation of heat flow with dP/dt when the anomalous heat appeared

3.3 TLD results－a nuclear origin of the heat flow ?

The thermoluminescence dosimeter (TLD) is a detector that can absorb the energy of the ionizing radiation and remember the dosage of radiation in terms of the energy of excitation; then, it will release the energy of excitation as a visible light when TLD is heated later after being radiated. The TLD used in our experiment is only sensitive to the radiation which energy-ranges from 30keV to 3Mev. Table 4 gives the results of TLD detection in reaction and reference vessels, respectively.

Table 4 Dosage difference of radiation between reaction and reference vessels

System	Average Dosage (10^{-6}Gy)		△ Dosage (10^{-6} Gy)	Calibration coeff.. (10^{-7} Gy/TL)	Experiment cycle(s)
	reaction vessel	reference. vessel			
D-Pd	3.8	2.9	0.8	1.11	once
	13.7	11.3	2.4		5
	3.7	2.6	1.1	0.84	once
N-Pd	9.7	10.0	-0.3		once

From the Table 4, we may learn that the dosage absorbed by TLD in reaction vessel is obviously higher than that in reference vessel. That means that the energy of some radiation in the reaction vessel must be higher than 30keV. When the experiment was repeated once and once again while TLD was kept inside the reaction vessel intact, the difference of dosage between reaction vessel and reference vessel increases with the number of cycles (row 2 in Table 4). Hence, the anomalous heat flow might come from a nuclear origin, because the energy released from the chemical process will usually be in the range of several or tens of eVs. In nuclear reaction the nuclei as reactant will fission or fuse into some new nucleus; in addition all of electrons outside the nucleus will rearrange completely. So the energy released from a nuclear process will at least be several keV. Its maximum can reach some mega-eV or more. The radiation of more than 30keV found in our system implied a nuclear origin of heat flow. However further investigations are needed to confirm this nuclear process

4. CONCLUSION AND SUGGESTION

4.1 Deuterium flux caused by the permeation process through a Pd lattice may be a pre-requisite condition for a gas loading D-Pd system to go into an anomalous state. The anomalous heat flow can be detected only when the deuterium permeation appear.

4.2 The anomalous heat flow appears only when the temperature of Pd tube is decreasing. The temperature gradient in radial direction of Pd tube might help the resonant permeation of deuteron. The more attention should be paid to the decreasing rate of Pd temperature in future researches.

4.3 The fatigue effect: The amount of the anomalous heat was getting less and less when the experiment was repeated once and once again; the deformation of Pd lattice caused by the introduction of deuteron might be the important factor. This fatigued Pd can be resumed later.

4.4 TLD has detected a weak signal near the Pd tube. It implied a nuclear origin of heat flow, because the TLD is only sensitive to high energy radiation (>30keV)

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