Examinations of Errors in a D/Pd Gas-loading System when Using a Heat-flow Calorimeter

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Abstract. Measurement of a reaction between deuterium (hydrogen) gas and materials using a calorimeter which is calibrated by nitrogen will show erroneous excess heat power production due to the structure of the reaction chamber and the difference of thermal conductivity of the gases used in the calibration and triggering experiments, which leads to the energy generated in the chamber of the calorimeter has not been totally measured. The error is not obvious at low applied power, and it increases significantly with the increase of applied power. This insidious error is discussed by using a stable heat-flow (Seebeck) calorimeter and procedures to reduce error are put forward. And the authenticity of Rossi's patent is questioned.

1. Introduction

The abnormal phenomenon that solids containing deuterium (hydrogen) could be released excess heat exceeding chemical energy in the field of condensed matter nuclear science continues to attract the attention and research [1,2] from scientists since 1989 [3]. For the existing or newly proposed theories do not match with experimental results well, instability and unsatisfactory repetition rate of experimental results have caused many scientists to hold pessimistic and negative attitudes [4,5] towards the research. In 2011, A. Rossi published the H/Ni system patent [6] that could produce a usable excess heat, which had a great impact internationally.

In previous work [7,8], approximately one hundred watts of excess heat was measured in a deuterium/palladium gas-solid system by using an isothermal calorimeter. Since the experimental results were only calculated by the temperature difference between the inside and outside of the system with the method of isothermal calorimetry, they were greatly affected by the external environment, resulting in significant errors. Therefore, a large volume and high power heat flow calorimeter [9] (HFC) was introduced into the system and watt-level excess heat was measured [10]. However, in the subsequent analysis, it was found that due to the structure of the reaction chamber and the different thermal conductivities of the gases used in the calibration and triggering experiments, the energy generated in the calorimeter was not completely sensed and measured, and further analysis and discussion on the measurement errors were discussed here.

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2. Experimental

The experimental system and consumables are detailed in the previous work [10]. The schematic diagrams of the heat-flow calorimeter and the experimental system are given, as shown in figure 1 and figure 2.





Figure 1. Schematic diagram of the system.

Figure 2. Schematic diagram of the heat-flow calorimeter.

Among them: 1_circulating water bath inlet/outlet of reaction chamber; 2_reaction chamber (isothermal calorimetry); 3_transition chamber; 4_capacitance gauge (INFICON CDG025D); 5_inlet/outlet valve; 6_gate valve; 7_turbo molecular pump; 8_mechanical vacuum pump; 9_reaction chamber (heat-flow calorimetry); 10_aviation plug, external connected with Keithley 2700 data acquisition system; 11_ large volume and high power heat-flow calorimeter.

2.1. Calibration and Triggering Experiment

In the first round of experiments, in order to avoid other metals that might affect the experimental results, palladium wire was used as the heating wire and experimental wire of the experimental system. After pumping reaction chamber to a high vacuum, the system was calibrated with nitrogen gas at 1 atm. The calibration equation was:

$$P_{in} = (14.160 \pm 0.044)V - (0.011 \pm 0.002)V^2 \tag{1}$$

In the triggering experiment, the palladium wire was repeatedly charged and discharged with deuterium under different current (temperature). It was found that after several experiments, the palladium wire was broken. Because of the high resistivity of palladium wire, the heat generated by the heating palladium wire would cause the temperature at the aviation plug to be higher. As a result of that, a certain amount of energy escaped out of the calorimeter before measurement. In order to increase the heating efficiency and reduce the experimental cost, in the subsequent experiments, the heating palladium wire was replaced by a copper wire and a resistance wire. The resistance wire was wound on the ceramic tube in the reaction chamber, and the copper wire was used to connect the resistance wire to the aviation plug. Compared with palladium, copper had a much lower resistivity and the current thermal effect was not obvious. After replacing the heating wire, the system was calibrated with nitrogen gas. The calibration equation was:

$$P_{in} = (13.504 \pm 0.024)V - (0.013 \pm 0.001)V^2 \tag{2}$$

After that, several triggering experiments were carried out under different pressures and different input powers. The main experimental results were shown in table 1. From the experimental results, the excess heat generated by the system significantly reduced. After replacing the heating wire from palladium to copper, less heat energy escaped out of the system. But in the calibration and triggering experiments, the heating wires had not been until the experiments ended. For what reason, the excess heat power reduced from ten-watt level to about one watt. It was also suspected that the different

thermal conductivity of the gas used in the calibration and triggering experiments affected the experimental results.

Pressure(kPa)	$P_{in}(W)$	$P_{ex}(W)$
89	401.01	1.11
91	325.85	0.01
55	422.95	0.98
56	325.73	-0.24
32	252.68	-0.36
4.7	396.51	1.68
0.15	267.57	0.53
0.11	205.36	0.85

Table 1. Triggering results under different pressure.

2.2. Using Different Gases for Calibration Experiments

In order to verify whether the difference in thermal conductivity of the gas caused the system measuring spurious excess heat, the experimental palladium wire in the system was removed, and hydrogen and nitrogen gas were selected for calibration experiments. The thermal conductivity of hydrogen and nitrogen at 0 °C are 0.163 and 0.023 W / (m · °C), respectively. The thermal conductivity of gas is less affected by pressure. Since the thermal conductivity of hydrogen and nitrogen are quite different, the influence of pressure on the thermal conductivity of gas was ignored. The relationship between temperature and thermal conductivity of hydrogen and nitrogen are shown in figure 3 and figure 4.



Figure 3. Thermal conductivity of hydrogen.

Figure 4. Thermal conductivity of nitrogen.

Due to the limitations of the experimental system, whether it is a calibration experiment or a triggering experiment, the maximum temperature in the reaction chamber will not exceed 500 °C, and the gas pressure in the reaction chamber will not exceed 1.5 atm. It can be concluded from figure 3 and figure 4 that in the experiment, regardless of the conditions, the thermal conductivity of hydrogen will be greater than that of nitrogen. The system was calibrated by 1 atm hydrogen and nitrogen respectively, and the calibration equations of the system are as follows:

H₂:
$$P_{in} = (13.504 \pm 0.015)V - (0.013 \pm 0.001)V^2$$
 (3)

N₂:
$$P_{in} = (13.554 \pm 0.024)V - (0.016 \pm 0.002)V^2$$
 (4)

Put the two equations into the same coordinate system, the relationship between them was shown in figure 5 (partial enlargement).

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Figure 5. Relationship between thermal power and the voltage generated by the THC.



Figure 6. Thermal power difference of the calibration equations (eq.3 minus eq.4).

It can be seen that the calorimeter needs to obtain the same thermo electromotive force, and the required input power under the nitrogen calibration is more than that under the hydrogen calibration. Conversely, when hydrogen is used to trigger the experiment, the power required to achieve the same thermo electromotive force is smaller. And this part of the power difference is misunderstood as the excess heat power released by the system. Subtract the calibration equation of hydrogen from the calibration equation of nitrogen to obtain the relationship between the calorimeter thermal electromotive force and the calibration power difference (erroneous excess heat power), as shown in figure 6. It can be seen that as the electromotive force (input power) of the calorimeter increases, this calibration power difference (error) also increases, that is, the "excess heat" power of the system also increases. It can be considered that the "excess heat" power calculated in the trigger experiment is an unreal result.

3. Analysis and Discussion

In an ideal calorimeter, the heat released inside the calorimeter will be fully absorbed and measured. However, in actual situations, the calorimeter will always be unable to collect the internal heat completely for some reasons, causing part of the heat escaping out of the system before the measurement. A high-precision calorimeter will try to reduce this part as less as possible.

Due to the structure of the reaction chamber (calorimeter) and the differences of the thermal conductivities of the gases used in the calibration and triggering experiments (nitrogen and deuterium respectively), the chamber will have different temperature gradient and the generated energy will not be totally measured. The different temperature gradient leads to errors when calculating the excess heat power using isothermal calorimetry. In the heat-flow calorimeter, this part of energy will be misunderstood as excess energy due to heat escaping. It can be concluded from the experimental data that at low input power, this difference is not obvious, but as the input power increases, this difference is magnified significantly. Due to the limitations of the experimental equipment, it is impossible to input higher power to verify this conjecture.

In Rossi's patent, only air is used for calibration experiment, hydrogen is used for triggering experiments, and isothermal calorimetry is used to calculate the "excess heat" power of the system. From the patent, as the energy consumption increases, the energy produced by the system also increases. This is consistent with the conclusion obtained from previous experiments results. It is reasonable to believe that Rossi did not consider the measurement error caused by the difference in thermal conductivity of the gases at the time.

Energy can be moved from the place where the energy is generated through the gas to another place and escape out of the system before the measurement. If calibrating such a calorimeter with a gas that is different from the research gas, such as, when studying the behaviors of hydrogen,

calibrating with nitrogen, due to the difference in thermal conductivity of the two gases, obvious additional energy generated will be measured. In other words, no matter how the temperature is measured, as long as the heat escapes from the calorimeter before the measurement, the same error will occur. And it can be concluded through experiments that the accuracy of the calorimeter is sensitive to the thermal conductivity of the gas in it. Through experiments, we have learned the cause of this error, and the following process can be used to reduce the error:

1) When there is no sample or inert materials, the calorimeter is calibrated with nitrogen and hydrogen respectively.

2) In the triggering experiment, compare the results with the nitrogen calibration results. If no changes are observed, the calibration results based on nitrogen can be used. If the results change, the calibration based on hydrogen can be used.

3) Use a gas with a thermal conductivity similar to the gas used in the trigger experiment for the calibration experiment, such as helium.

4. Conclusion

Because gases with different thermal conductivity are used in the calibration experiment and the triggering experiment, when the calibration result of nitrogen is used, the calorimeter will produce a significant error when measuring the reaction involving hydrogen (deuterium) gas. This error can be misunderstood as excess heat energy produced by the system, and it increases as the input power (temperature) increases. The excess energy measured in the Rossi patent was questioned. Using a gas with a thermal conductivity similar to that of the triggering gas for calibration can reduce such errors.

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