INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS

J. Phys. D: Appl. Phys. **36** (2003) 3095–3097 PII: S0022-3727(03)65341-6

Correlation between abnormal deuterium flux and heat flow in a D/Pd system

Xing Zhong Li[1], Bin Liu[1], Jian Tian[2], Qing Ming Wei[1], Rui Zhou[3] and Zhi Wu Yu[3]

[1] Department of Physics, Tsinghua University, Beijing 100084, People's Republic of China
[2] School of Life Science, Changchun University of Science and Technology, Changchun 130022, People's Republic of China
[3] Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

Received 26 June 2003
Published 19 November 2003
Online at stacks.iop.org/JPhysD/36/3095

Abstract
Deuterium flux through the thin wall of a palladium tube has been studied by monitoring gas pressure and temperature. A high-precision calorimeter (Calvet) was used to detect heat flow when the heater was shut down and the palladium tube was cooling down slowly. At certain temperatures an abnormal deuterium flux appeared. This deuterium flux reached a peak when the temperature of the palladium was decreasing. This abnormal deuterium flux differs from the monotonic feature of a normal diffusive flux and is accompanied by a heat flow.

1. Introduction

Palladium tubes have normally been used as filters of hydrogen (deuterium) gas to attain the highest purity because hydrogen (deuterium) gas has a greater diffusion coefficient through palladium than that of any other gas [1, 2]. This diffusion coefficient dramatically increases when the temperature of the palladium increases [3, 4]. Hence, the palladium tube is usually heated to red heat in order to switch on an instant source of pure hydrogen (deuterium) in experiments (such as gas discharge devices, ion sources for accelerators, etc). Hence temperature variation was not examined when the hydrogen (deuterium) was passing through the thin film of the palladium tube. However, when we studied the calorimetric behaviour of the deuterium/palladium system, an unexpected phenomenon was observed of temperature rising unexpectedly when the hydrogen (deuterium) gas was pumped out from the palladium wire. As the hydrogen (deuterium) leaving from the palladium wire was believed to be an endothermic process, we expected to observe a temperature drop when the hydrogen (deuterium) gas started to leave the palladium wire. In one series of experiments, the palladium wire was heated by an electrical current flow inside the palladium wire; hence, the temperature rise might have been caused by several effects such as the change in the electrical resistance of the Pd wire, and/or variation of the heat transfer coefficients. We therefore decided to use a Calvet calorimeter to detect this exothermic effect because the Calvet calorimeter is based on the Seebeck effect, which does not rely on heat transfer coefficients. In this new series of experiments, not only was this exothermic effect confirmed, but it was also correlated with the deuterium flux permeation of the thin film of palladium.

2. Apparatus

Figure 1 shows a schematic view of the apparatus in this experiment with a thin palladium tube plugged into the reaction vessel of a Calvet calorimeter, which is composed of a series of thermal couples and by two reaction vessels (only one of which is shown in figure 1). These thermocouples encircle the reaction vessel in order to detect any heat flow from any

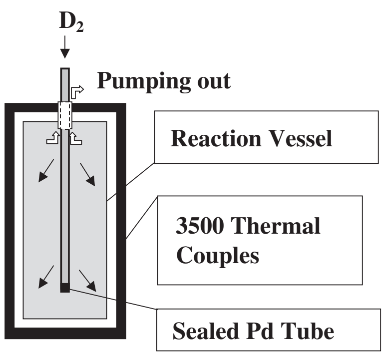

Figure 1. Schematic view of the high-precision calorimeter (Calvet C-80 D).

heat sources within the reaction vessel. In order to increase precision, two identical vessels are arranged symmetrically and are connected electrically in series in reversed polarity in order to cancel the effect of the environment due to fluctuation in the ambient temperature. This palladium tube (26 mm $\times$ 0.1 mm $\times$ $\varnothing$4 mm) is sealed at one end, and deuterium gas is fed through the other end. The reaction vessel is pumped by a vacuum pump through the co-axial tube at the top of the reaction vessel in order to generate a pressure difference across the thin wall of the palladium tube. The deuterium flux through the thin wall is very low because the diffusion coefficient of hydrogen (deuterium) gas in palladium at room temperature is quite low. The Calvet calorimeter has been designed to heat the two vessels homogeneously using heaters embedded in the insulator surrounding the two vessels. This Calvet calorimeter (C-80D) was imported from a French company (Setaram), and it is designed to be sensitive to a heat flow of 1 μW, and it has been calibrated with a standardized vessel equipped with a standard electrical heater. When we heated the vessels and the tube, the deuterium flux across the thin wall of the Pd tube gradually increased. This deuterium flux was monitored by the pressure in the reaction vessel while the pump still kept running. All data for pressure, heat flow, and temperature were recorded by a data acquisition system controlled by a computer. When the electrical heaters embedded in the insulator were switched off, the temperature of the system decreased gradually. Since the C-80 Calvet calorimeter is well insulated in a big cylindrical insulator, the cooling process was very slow. It usually took about 10 h to cool the system from 250°C to 70°C.

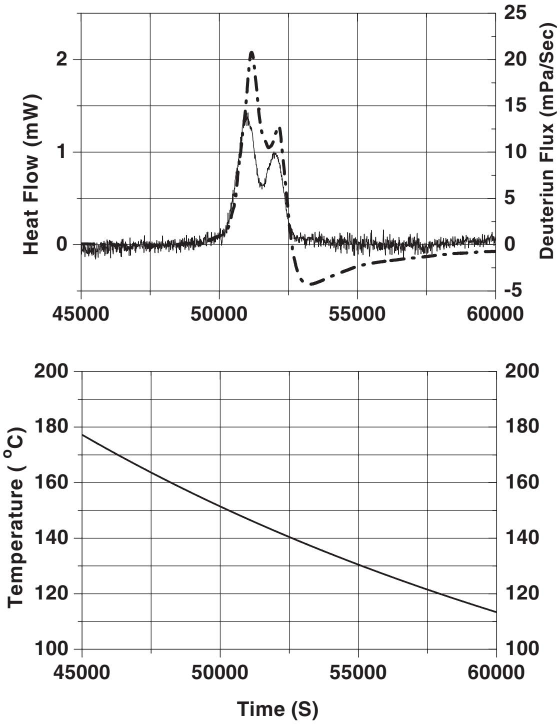

Figure 2. Correlation between deuterium flux and heat flow; dash-dot-dash line shows the heat flow: solid line in the upper plot shows the deuterium flux across the thin wall of the palladium tube; solid line in the lower plot shows the temperature of the palladium tube.

3. Results

Figure 2 shows the results of one of the experiments. The Calvet calorimeter (C-80D) was first uniformly heated to 200°C by the heater. Deuterium was then fed into the palladium tube inside the reaction vessel. After half an hour, the heater was switched off. While the reaction vessel was cooling down, the vacuum pump was working continuously in order to pump out the permeating deuterium gas. The D_2 pressure inside the Pd tube was about 1.4 atm. The permeation rate was low; hence, the pressure in the vessel was about 150 Pa. When the temperature approached $\sim$150°C (see the lower plot in figure 2), the pressure in the reaction vessel started increasing quickly although the pump was still working continuously. At the same time the Calvet calorimeter recorded a heat flow (shown by the thick dash-dot-dash line in the upper plot of figure 2). We then calculated the derivative of the pressure with respect to time ($\mathrm{d}P/\mathrm{d}t$) in order to monitor the deuterium flux permeating the thin wall of the Pd tube. When this deuterium flux reached a peak (shown by the thin solid line in the upper plot of figure 2), the heat flow also showed a peak. When the temperature decreased further, the deuterium flux decreased to a valley while the heat flow also showed a valley. After the first peak of deuterium flux, there was a second peak before 140°C, and the heat flow reached its second peak in parallel. We carefully calculated the deuterium flux in order to consider the effect of the continuous pumping, and we obtained the two peaks of the deuterium flux as shown by the thin solid curve in the upper plot of figure 2. There was a small time delay between the two sets of peaks. The peaks of the deuterium flux appeared a little earlier than the peaks of the heat flow. The time delay is about 240 s, and the time constant of the Calvet calorimeter is just about 250 s. When the temperature was lower than 140°C, the deuterium pressure inside the vessel started dropping because the deuterium flux diminished. The negative value of the heat flow in figure 2 indicated an endothermic effect just after the deuterium flux had stopped. Probably, it had been caused by a desorption process in the reaction vessel due to the dropping of D_2 pressure inside the vessel. This correlation between deuterium flux and the heat flow was confirmed 16 times with the same palladium tube under various D_2 pressure differences.

4. Discussion

(1) Permeation of deuterium through the thin wall of a palladium tube has been supposed to be a diffusion process, and the deuterium flux assumed to be a monotonic function of temperature, with the diffusion coefficient of deuterium gas inside the palladium decreasing when the temperature decreases. However, what we observed was a different, up and down trend. Moreover, it showed a double peak structure that is not expected if the diffusion coefficient, D, had followed the conventional expression as in [5]:

$$D = D_0 \exp\left[-\frac{E_a}{T}\right] \tag{1}$$

Here, D_0 and E_a, are two constants; T is the temperature in Kelvin. It seems that there may have been some kind of resonant process involved in the abnormal double peak structure.

(2) This abnormal deuterium flux with a double peak structure seemed correlated with an exothermic process. We might think of solution of deuterium into the palladium, and the formation of deuteride inside the palladium, because both these processes are exothermic. In order to check if this was true, deuterium gas was fed into both sides of the Pd wall (i.e. the reaction vessel and the palladium tube) and the experiment run again. In this case, heat flow was not observed when the temperature of the palladium tube passed through the particular temperature region. Hence, the deuterium flux permeating the thin wall of the palladium tube must be an important factor for this heat flow. We might assume that this resonant process enhances the concentration of the deuterium atoms inside the palladium lattice, where it enhances the flux permeating the thin wall of the palladium tube. Such a plausible assumption seems supported by the dip after the double peak structure of heat flow in figure 2. After 52 500 s, the deuterium flux entering inner surface of the Pd tube approached zero; hence, the continuous pumping in the reaction vessel was no longer balanced by the influx of the deuterium. Thus the density of deuterons inside the wall of the palladium tube was decreasing. Consequently, dissolution and desorption on the outer surface of the Pd tube at the reaction vessel side could not be balanced by the absorption and solution on the inner surface of the Pd tube. Both the dissolution and the desorption are endothermic processes that would cause the dip after 52 500 s.

(3) Joule–Thomson effect? When we tried to find the source of this heat flow, at first glance, there was a possibility of the Joule–Thomson effect because the thin wall of the palladium tube might be considered as a porous partition, and the inversion temperature for hydrogen is 205 K. However, this seemed impossible after qualitative consideration. The Joule–Thomson effect is important only for high-pressure and low-temperature gases that are far away from an ideal gas. In our experiment the gas pressure was less than 2 atm, and the temperature was higher than 393 K, so that the Joule–Thomson effect is negligible. In particular, the deuterium flux is very low (of the order of milliamperes), so that based on the Joule–Thomson coefficient for hydrogen ($-0.023\,31$ K atm^{-1}), we may show that the heating power due to the Joule–Thomson effect for our case is much less than 1 μW, which is negligible.

(4) Self-sustaining. It would be interesting if we were able to maintain the temperature of the D/Pd system at a specific point, say 150˚C, by the heat flow itself. We might then keep this exothermic process in a self-sustaining steady state. A new system has been designed to test this idea, and preliminary results are encouraging.

Acknowledgments

This work is supported by The Ministry of Science and Technology (Fundamental Division), Natural Science Foundation of China (#10145004) and Tsinghua University (Basic Research Fund (985-I)).

References

[1] Graham T 1866 *Phil. Trans. R. Soc.* **156** 415
[2] Lewis F A 1966 *Palladium/Hydrogen System* (New York: Academic) p 3
[3] Alefeld G and Volkl J 1978 *Hydrogen in Metals, I, Basic Properties* (Berlin: Springer) p 325
[4] Alefeld G and Volkl J 1978 *Hydrogen in Metals, II, Application-Oriented Properties* (Berlin: Springer) p 73
[5] Fukai Y 1993 *The Metal–Hydrogen System, Basic Bulk Properties* (Berlin: Springer) p 230