

Excess heat release during deuterium sorption-desorption by finely powdered palladium deuteride

V. A. KIRKINSKII(*), V. A. DREBUSHCHAK and A. I. KHMELNIKOV

*Institute of Mineralogy and Petrography
Siberian Branch of the Russian Academy of Sciences
prospect Acad. Koptyuga, 3, Novosibirsk, 630090, Russia*

(received 2 May 2001; accepted in final form 30 January 2002)

PACS. 81.70.Pg – Thermal analysis, differential thermal analysis (DTA), differential thermogravimetric analysis.

PACS. 25.45.-z – ^2H -induced reactions.

Abstract. – Thermal effects have been studied in the course of sorption-desorption of hydrogen isotopes by a finely powdered palladium deuteride using a differential scanning calorimeter DSC-111 SETARAM. During α - β transition an excess heat release is observed in palladium deuteride of about one watt per gram of deuteride. In similar experiments with palladium hydride no anomalous effects have been observed. On the basis of earlier computer modelling, relevant publications and our experimental results, the excess heat release during deuterium sorption-desorption by palladium deuteride is attributed to the fusion reactions of deuterium atoms yielding helium.

Measurements of thermal effects during electrolysis of solution based on heavy water (deuterium oxide) making use of palladium electrodes have been published in over 100 works (see reviews [1–5]). Some authors reported the excessive heat release as compared with the energy consumption by the electrolysis. The heat release was tentatively attributed to the fusion reactions yielding mainly helium. This viewpoint was, however, severely criticised. The reliability of experimental results was questioned because the technique of calorimetric measurements in electrochemical cells is sometimes not free from serious flaws. Recently, new results have been published (*e.g.*, a series of publications [6]) but whether any excess energy is released under the deuterium interaction inside a palladium cathode along with the energy output due to usual physical and chemical processes remains an open question.

According to the earlier theoretical computations [7, 8] and to the analysis of the available experimental data, phase transitions in palladium deuteride must be accompanied by measurable energy generation due to the fusion reactions.

In order to exclude the errors inherent in calorimetric measurements of electrochemical processes, we have developed a special procedure for the measurements of the excess heat release in the palladium deuteride based on the comparison of thermal effects during hydrogen

(*) E-mail: kirkinsk@uiggm.nsc.ru

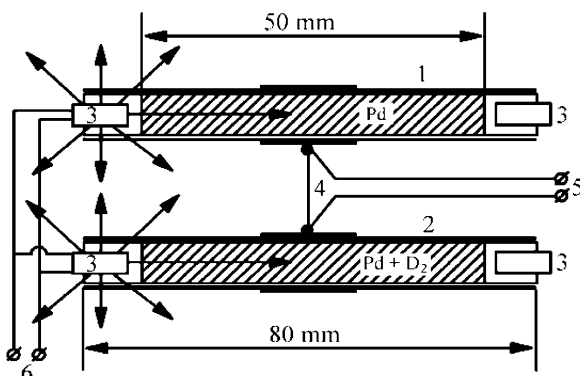


Fig. 1 – Schematic diagram of calorimetric measurements: 1) reference ampoule; 2) measured ampoule with the substance; 3) heaters; 4) calorimetric detector (thermocouples batteries); 5) calorimetric signal measurement amplifier; 6) power supply for the heaters. The arrows designate a heat flow from heaters on the left side of the ampoules in the “on” condition.

isotopes sorption-desorption by palladium employing a commercial calorimeter DSC-111 SETARAM [9]. The procedure implies that the signal detected by the calorimeter at the heat input changes if additional sources of energy release are in the sample. If only reversible processes occur in the sample, the heat registered by the calorimeter will practically linearly depend on the applied electric power. If the electric pulse activates the excess heat production due to internal sources, the signal dependence on the heat released on the heater must be non-linear.

Measurement methods. – A hermetically sealed steel ampoule with the studied substance was placed into the measuring channel of the calorimeter, an identical ampoule with Pd powder was placed symmetrically in a reference channel (see fig. 1). The composition of the studied substances and the experimental conditions are shown in table I.

To prepare Pd powder, we treated a PdCl_2 solution with sodium formiate $\text{Na}(\text{HCOO})_2\text{H}_2\text{O}$. The precipitate was filtered off on an ash-less filter, washed by alcohol and then ignited. Scanning electronic microscope JSM-35 showed that Pd particles range in sizes from 100 to 800 nm but over 70% of them range in size from 300 to 500 nm and are isometrically shaped.

Palladium deuteride $\beta\text{-PdD}_x$ was obtained by charging a $5\ \mu\text{m}$ thick Pd foil (99.9% pure)

TABLE I – Content of the ampoules with the studied substances and conditions for Series 1–8 of experiments.

No.	Content of ampoule	T (K) ^(a)	Number of cycles
1	Foil $\text{PdD}_{0.6}$ (0.3g) + powder Pd (0.3g)	440	9
2	Foil $\text{PdD}_{0.6}$ (0.3g) + powder Pd (0.3g)	440	8
3	Foil $\text{PdD}_{0.6}$ (0.3g) + powder Pd (0.3g)	520	9
4	Foil Pd (0.3g) + powder Pd (0.3g)	440	8
5	Foil $\text{PdH}_{0.6}$ (0.3g) + powder Pd (0.3g)	440	10
6	Foil $\text{PdH}_{0.6}$ (0.3g) + powder Pd (0.3g)	295	10
7	Foil $\text{PdH}_{0.6}$ (0.3g) + powder Pd (0.3g)	440	10
8	Foil $\text{PdH}_{0.6}$ (0.3g) + powder Pd (0.3g)	400	10

^(a)The temperature is indicated in the center of the calorimeter prior to electric pulse.

with deuterium in the course of electrolysis of heavy water containing 0.1 M LiOH at the current density of 50 mA/cm² for 70–100 hours. The heavy water (99.9% D₂O) had been produced by the Experimental Plant of the State Institute of Applied Chemistry, St. Petersburg. The completeness of transformation into the β -phase and its composition was controlled by the weight and X-ray methods using a diffractometer. The composition of the obtained palladium deuteride corresponded to PdD_{0.60±0.01}. Making use of lithium hydroxide produced an insignificant amount of light hydrogen isotope as an impurity with H/D ratio about 1:300. Palladium hydride was obtained by a similar technique but doubly distilled H₂O was used in the electrolysis.

Equal masses of palladium deuteride (or hydride) foil and Pd powder were placed in the measured ampoules. The ampoules were hermetically sealed by press-fitted copper ring. They were kept at 650 K for 30 minutes to force the foil to desorb hydrogen isotopes. Then the ampoules were cooled down to room temperature to provide the sorption of a gas with finely powdered palladium whose surface is much greater than that of the foil. The weight method was used to control the absence of gaseous hydrogen isotopes losses. The calorimeter measurements showed that the sorption-desorption of hydrogen isotopes resulted in the temperature range of 450–500 K. One and the same reference ampoule with pure palladium powder was used in all experiments performed.

Platinum wire heaters with an approximately equal resistance of ≈ 2.7 ohm were placed on the ends of the ampoules. Power from a.c. generator was alternately supplied to the right and left heaters. The electric energy released on the heaters was calculated from the readings of voltmeter and amperemeter. Prior to starting the measurements, the ampoules were centred one at a time in the channels so that the heat flows from equal electric pulses of the left and right heaters were equal. At constant temperature and when the heaters were switched off, the calorimetric signal is constant. On measurements taken at elevated temperature, the temperatures at the centre and at the ends of the channel and, therefore, of the ampoule, are different.

The heat flow measured by the calorimeter is only a part of the supplied electric power: $W = I \cdot V \cdot \alpha$, where I is the current, V is the voltage and α is the calibration coefficient measured by us as a function of the distance between the heater and the detector.

After both the ampoules have been centred, the heaters are connected into circuit. When the current is on, the calorimeter measures the difference between the signals from the measured and reference ampoule. The measurements are performed in the following way. At the initial stationary state, at constant heat flow, the heaters are switched on for 300 seconds. The current and voltage are measured at the 100th and 200th seconds. The heat flow attains a new constant value. In 300 seconds, the heaters are switched off. This brings the heat flow back to its original state in 250–400 seconds (depending on the pulse power). Then the heaters at the opposite side of the ampoule are switched on and the procedure is repeated. After the signal has been brought into its original state, a new cycle begins. The voltage is increased by about 50%.

Experimental results. – Eight series of experiments have been carried out (see table I). The data for Series 7 (with palladium hydride) are presented in figs. 2 and 3. It is evident that the recorded signal retains its form and increases linearly with the increase in pulse power. The similar linear signal dependence on the electric power applied to the heaters has been observed in Series 5–8.

A completely different type of dependence occurs when palladium deuteride is used. By way of example, consider the results of Series 2. On power increase to 3 W, the measured signal increases. As the power is increased further, the measured signal falls and even its

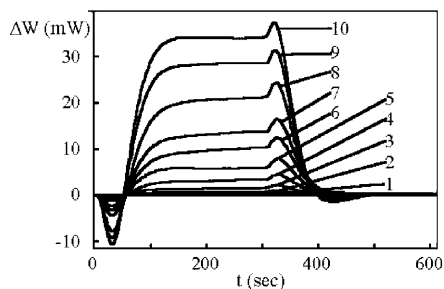


Fig. 2

Fig. 2 – The change in the form of the signal detected using the palladium hydride under changing supplied power in cycles 1–10 for Series 7 (watt): 1) 0.13; 2) 0.28; 3) 0.64; 4) 1.30; 5) 2.3; 6) 3.2; 7) 4.3; 8) 7.1; 9) 8.8; 10) 10.2.

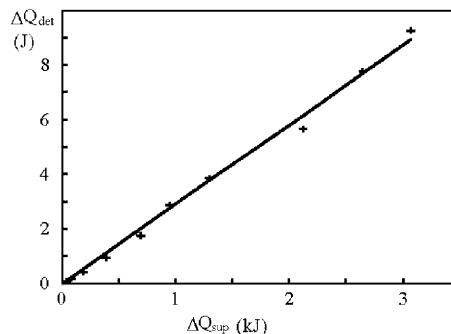


Fig. 3

Fig. 3 – Heat detected by the calorimeter (ΔQ_{det}) on the ampoule with the palladium hydride (Series 7) *vs.* supplied electric heat (ΔQ_{sup}).

sign is changed. The experimental results for all the eight cycles are shown in figs. 4 and 5. Anomalous dependence of the calorimetric signal value on the applied pulse was observed with the same sample after a lapse of two months at the temperatures of 440 and 520 K.

Discussion. – The obtained results show that during deuterium sorption-desorption by the finely powdered palladium deuteride, excess energy is released whereas in the analogous experiments with the light hydrogen isotope no anomalous effects have been observed. The experimental conditions (hermetically sealed ampoules with the sample inside, the ampoule mass conservation after the experiments, similarity of measurement procedure on using deuteride and palladium hydride) make it impossible to attribute the obtained difference to chemical

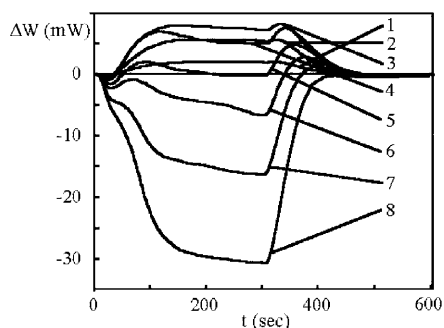


Fig. 4

Fig. 4 – The change in the form of the signal detected using the palladium deuteride under changing supplied power (ΔQ_{sup}) in cycles 1–8 for the Series 2 (watt): 1) 0.37; 2) 1.33; 3) 2.62; 4) 4.5; 5) 5.5; 6) 6.5; 7) 8.9; 8) 11.6.

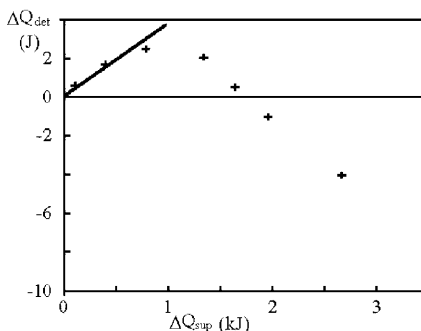


Fig. 5

Fig. 5 – Heat detected by the calorimeter (ΔQ_{det}) on the ampoule with the palladium deuteride (Series 2) *vs.* supplied electric heat (ΔQ_{sup}).

grounds or various D and H diffusion rates in the palladium. The source of the excessive heat release can be mainly the fusion reaction of the deuterium atoms yielding helium with absorption of the released energy by the palladium deuteride: $D + D \rightarrow {}^4\text{He}$. Contrary to the high-energy experiments, ${}^3\text{He}$ is produced in less amounts according to the reaction $D + D \rightarrow T + p$ with subsequent decay of tritium: $T \rightarrow {}^3\text{He} + \beta$. Another reaction, $D + D \rightarrow {}^3\text{He} + n$, is less probable [10]. The mechanism of fusion energy absorption by a crystalline structure and the reason of radically different branching ratio for D + D fusion in condensed media at low energies and in charge particle accelerators at high energies have been widely discussed in the literature (see, *e.g.*, [10–18]) and will be treated by us separately.

The computer modelling [7, 8] of deuterium atoms interaction in the palladium also confirmed a significant increase in the rate of the nuclear interaction of deuterons in the crystalline structure of the palladium deuteride with the rise in their mobility due to the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ phase transitions. The relation between the fusion reactions and phase transitions in metals was the basis of the invention [19, 20].

An important factor favourable for the intensification of the fusion reaction is making use of palladium powder with the minimum particles size [6, 19, 20]. In this case the maximum D/Pd ratio in particles increases which enhances the probability of deuterons approaching closely each other. Furthermore, the mass of palladium deuteride undergoing the phase transformation at a time unit varies proportionally with the general surface area of particles.

The maximum release of excess energy recorded by us in Series 1-2 is estimated as 10 joules which, taking into account the conditions of our experiments (mass of $\text{PdD}_{0.6} = 0.3$ g, $t = 300$ seconds and coefficient $\alpha \approx 0.1$), corresponds to ≈ 1 watt of excess output power per gram of palladium deuteride. The order of magnitude of this value corresponds to the earlier performed theoretical evaluations of the fusion reaction rate in palladium deuteride [7, 8].

Similar results had been obtained earlier in [6] by the electrolysis of the solution on the basis of D_2O when the closed palladium ampoule with the finely powdered palladium deuteride inside served as a cathode, *i.e.* under conditions in this respect similar to our experiments. In the series of experiments performed under various modes continuously for several thousand hours, an excess heat release has been observed with the power of 1.7–3.4 W/g. The analysis of gases accumulated in the ampoule after the experiment was performed on a high-resolution mass-spectrometer and showed significant content of helium with the proportion of isotopes ${}^4\text{He}/{}^3\text{He}$ down to ≈ 4 which differs drastically from their atmospheric content equal to $7.2 \cdot 10^5$ and therefore rules out the possibility of its penetration from the atmospheric air. In experiments conducted under similar conditions using ordinary water solutions neither excess heat release nor helium generation have been observed.

In conclusion, our experiments excluding the possible sources of errors in measuring energy balance in electrochemical studies together with the results obtained in [6] are the evidence of the heat release resulting from nuclear fusion during sorption-desorption and diffusion of deuterium in finely powdered palladium deuteride with the order of magnitude of about 1 watt per gram of palladium deuteride.

* * *

The authors would like to express their gratitude to S. V. LETOV, for performing electron microscope studies of finely powdered palladium, and V. S. PAVLYUCHENKO and S. N. FEDOROVA, for X-ray control of the samples. The work has been carried out with the support of the Russian Foundation for Basic Research, grant 00-05-65387.

REFERENCES

- [1] TSAREV V. A., *Sov. Phys. Usp.*, **339** (1990) 881.
- [2] TSAREV V. A., *Sov. Phys. Usp.*, **35** (1992) 842.
- [3] STORMS E., *J. Sci. Exp.*, **10** (1996) 185.
- [4] STORMS E., *Infinite Energy*, **6** (2000) 10.
- [5] CHECHIN V. A., TSAREV V. A., RABINOVITZ M. and KIM G. E., *Int. J. Theor. Phys.*, **33** (1994) 617.
- [6] ARATA Y. and ZHANG YUE-CHANG, *Proc. Jpn. Acad. B*, **70** (1994) 106; **72** (1996) 179; **73** (1997) 1; **74** (1998) 155, 281; *Jpn. J. Appl. Phys.*, **37** (1999) L1274; **38** (1999) L774.
- [7] KIRKINSKII V. A. and NOVIKOV YU. A., *Theoretical modeling of cold fusion*, preprint, Novosibirsk, 1998, p. 48.
- [8] KIRKINSKII V. A. and NOVIKOV YU. A., *Europhys. Lett.*, **46** (1999) 448.
- [9] DSC-111 as a part of the system TG-DSC-111 is described in <http://www.setaram.com/symmetri.html>.
- [10] SWARTZ M. R., *Fusion Technol.*, **31** (1997) 228.
- [11] HORA H., CICCHITELLI L., MILEY G. H., RAGHEB M., SCHARMANN A. and SCHILD W., *Nuovo Cimento D*, **12** (1990) 393.
- [12] HORA H., KELLY J. C., PATEL J. U., MILEY G. H. and TOMPKINS J. W., *Phys. Lett. A*, **175** (1993) 138.
- [13] PREPARATA G., *Fusion Technol.*, **20** (1991) 82.
- [14] PREPARATA G., *Trans. Fusion Technol.*, **26** (1994) 397.
- [15] FLEISCHMANN M., PONS S. and PREPARATA G., *Nuovo Cimento A*, **107** (1994) 143.
- [16] HAGELSTEIN P. L., *Fusion Technol.*, **23** (1993) 353.
- [17] HAGELSTEIN P. L., *Trans. Fusion Technol.*, **26** (1994) 461.
- [18] BRESSANI T., DEL GIUDICE E. and PREPARATA G., *Nuovo Cimento A*, **101** (1989) 845.
- [19] KIRKINSKII V. A., International Patent Application PCT/RU93/00174, publication number WO 94/03902 (1994).
- [20] KIRKINSKII V. A., Patent of the Russian Federation No. 2055656, Bulletin: Isobretenia i Tovarnie Znaki, 8, part 2 (1996) 267.