Conference Proceedings Vol. 33
«The Science of Cold Fusion»
T. Bressani, E. Del Giudice and G. Preparata (Eds.)
SIF, Bologna 1991

NEUTRON EMISSION AND SURFACE OBSERVATION DURING A LONG-TERM EVOLUTION OF DEUTERIUM ON Pd IN 0.1 M LiOD

HIROO NUMATA, RYUZO TAKAGI AND IZUMI OHNO Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku Tokyo152 Japan
KAZUTAKA KAWAMURA Institute of Research and Development, Tokai University, 1117 Kitakaname, Hiratuka259-12 Japan
SHIRO HARUYAMA Tokyo National College of Technology, Kunugida, Hachioji, Tokyo153 Japan

ABSTRUCT

Long-term electrolysis for well annealed thick Pd rods (9.0 and 21.2 mm ø) in 0.1M LiOD have been performed to examine anormalous phenomena; neutron emission and heat bursts. The count rate of neutron (CRN) bunched for 3 h showed no significant increase at low current densities. High CRN appeared a few days later after the current increased to 102.4 mA/cm^2 and the temperature was raised to 50°C. In two experiments CRN and neutron energy spectrum of 2.45 MeV was reproduced.

Metallographic observation showed two faults, blisters, cross slips and holes on Pd surface and a raw of defects in a recrystallized grain. Microstructural changes of Pd electrode during long-term electrolysis is discussed.

INTRODUCTION

Fleischmann and Pons[1] and Jones et al.[2] recently reported the evidence of a nuclear fusion in condenced matter which undergoes unusual deuterium loading by means of electrolysis in heavy water system or deuterium gas equilibration and intense desorption induced by changing physical parameters i.e.temperature in a gas tight chamber[3-4]. Although many studies are aimed to duplicate the precausor's results, they did not obtain their purpose. A few reports, however claimed that low level neutron emission was observed with respect to 2.45 MeV energy spectrum[5-9] and only one group reported F&P type huge heat bursts[10]. An important aspect of these reports is that either neutron or heat bursts was observed sporadically, as such effect sustained for microseconds or several days. It is suggested that the characterization of materials is important to improve reproducibility of an experiment, consequently approach shortly the mechanism.

In our preliminary experiment[11], where an annealed Pd cathode (9 mm ø x 10 cm long) was used, high neutron count rate and neutron energy spectrum of 2.45 MeV were observed. Afterwards, the second experiment have been performed to test reproducibility using the same experimental set-up except twice in diameter of Pd electrode. During a long-term electrolysis initially no significant count rate of neutron was observed, while high count rate of neutron appeared for several hours or days after increasing current density and temperature.

In this study, the evidence of neutron emission is further discussed in connection with an electrode potential, temperature and metallographic observation during a long-term electrolysis.

EXPERIMENTAL

Electrolyte-0.1MLiOD-D_2O solution was prepared by addition of Li_2O(Wako pure chemicals:95 %) into D_2O(Merk:99.8 %, CEA:99.8 %, Isotec:99.9 %). The concentration of LiOD alkaline solution was substantially increased in the course of electrolysis since small amount of 0.1MLiOD was poured into the cell every day to replenish the exhausted one. During a long-term electrolysis incremental fills were made with pure heavy water to minimize the effect of electrolyte concentration on the eletrochemical system.

Electrolytic cell-The experimental cell(content is about 130 ml) was made out of transparent quartz, which has a water jacket. The temperature of circulating water in the jacket was controlled at 40 and 50°C by Coolnics(Komatsu-Yamato Co Ltd.). The upper part of the cell was plugged by a silicone rubber stopper where working, reference and counter electrodes and the assemblies (addition tube and the guides of thermocouples) were mounted. The electrode potential was refered to the potential of dynamic type (α+β) PdD reference electrode. The guide of the counter electrode was served as for gas outlet port. Once adjusting geometrical position of these electrodes, it was fixed to the cell and the gap was throughly sealed with a silicone rubber resin. The working electrode was a thick Pd rod (Nilaco Co Ltd. 99.95 %). Pd material was cast into a high purity alumina tube in a flow of Ar. The as-cast Pd rod was out gassed for 20 h in a 10^{-6} Torr vacuum at 800°C.

Ti rod (3 mm ø) gold plated was served as an electrical leading. It is screwed into the upper end of the Pd electrode as shown in Fig.1. The working electrode was set reasonably centrally in the cylindrical space circumscribed by the counter electrode (mixed oxides of Pd and Rh). Details of the electrode treatment before loading are shown in Table 1.

Microscopic observation after electrolysis-Surface appearance of a specimen was observed by an optical microscope and SEM (JOEL model T-330 20 kV). Microstructure observation inside the electrode was made by sectioning the rod with traverse and radial directions. The crosssectional area was polished using 6μ diamond paste. Then, it was lightly etched by dilute hydrochloric acid for optical microscopic observation.

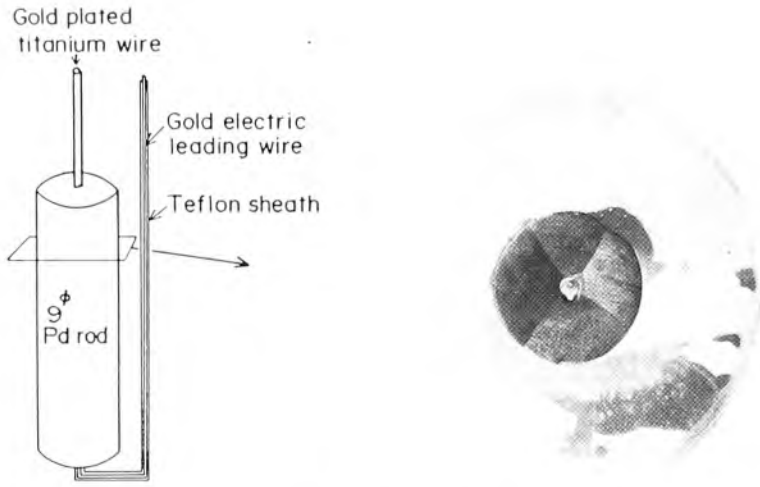


Fig.1 Schematic illustration of Pd electrode and optical micrograph of its crosssectional surface.

Table 1 Experimental conditions of Exp.1 and Exp.2; electrode dimention, pretreatment, current density.

Exp.1 ; Dimension of electrode $0.9^{\phi} \times 5.3^{\ell}$ cm Pd

Run No.	Current density mA cm-2	Pretreatments	Time/days
1st	0.05~40 40~500	Cast, 800°C annealing(10^{-6}Torr) acid treatment	Oct.16~Dec.20 1989
2nd	40	Polishing, acid treatment evacuation, Deuterium charge	Feb.16~Mar. 1 1990
3rd	40	Evacuation, polishing acid treatment	Mar. 1~Mar. 6
4th	40	Evacuation, polishing anodization	Mar.14

Exp.2 ; Dimension of electrode $2.1^{\phi} \times 3.2^{\ell}$ cm Pd

1st	0.05~ 102.4	Cast, 800°C annealing(10^{-6}Torr) Deuterium charge, acid treatment	Jul.20 1990 ~Feb. 1991

RESULTS AND DISCUSSIONS

We have performed two experiments (Exp.1 and Exp.2). In Exp.1 the Pd electrode was subjected to deuterium loading for two months, then the dilation of the electrode was ex-situ measured. The electrode was again pretreated (abrasion, degassing, D_2 loading and acid etching) before electrolysis and the above processes were repeated 4 times. The amount of adsorbed D_2 can be estimated by the variation of D_2 gas pressure. In Exp.2 deuterium loading had completed for 8 months without any interruption of electrolysis. The possibility of large neutron bursts has been examined in detail by monitoring the temperature and the overpotential (OP), so as to check a coincidental occurrence of neutron bursts and the increase of the temperature. Although the mechanism is still obscure, we used twice thicker Pd rod in Exp.2 considering Arata's suggestion[12].

OP and CRN of Exp.1

The galvanostatic cathodic current was applied on the Pd electrode, in which a current density was raised step by step from 0.05~102 mA/cm^2. The initial content of deuterium before electrolysis was estimated to be 0.36 in atomic ratio. At onset of a cathodic current the OP showed an irregular shift to noble direction, then it was reached at steady state value. At low current density it obeys the Tafel relation, which shows that the cathodic OP is a linear relation with the logarithm of a current density[13].

When the current density was increased to 40 mA/cm^2, significant count rate of neutron (CRN) above background was observed. However, this CRN did not last for a long time since it abruptly falled down to the background level somewhat later the current increase. This intermittent fluctuation of CRN was observed for several times ; 2nd~4th run followed by a current perturvation. This behavior of CRN was reproduced in Exp.2, as is shown below (see also Fig.5(c)). Menlove at al[3]. reported two different types of neutron emission from dueterium loaded Ti chips. It has become apparent that the bursts (200 μs) was occurred shortly during increasing temperature and the

intermittent weak neutron emission lasted for 12h after the temperature recovered. The latter intermittent CRN corresponds to our CRN fluctuation. On the other hands, large neutron bursts were not measured in Exp.1, which is sporadically appeared during intense desorption induced by discharge activation or temperature cycling. Interestingly the intermittent CRN (see also Fig.5 (c) and (d)) seems respond to the current on or temperature cycling, which suggests that cold fusion is induced by intense adsorption or desorption by electrochemical reaction or temperature cycling.

Energy spectrum during the period of high CRN in 1st run show the characteristic of 2.45 MeV neutron. We had carefully checked data with regards to the statistics, effect of cosmic ray, temperaure of the detector. The energytic neutron counted by an NE213 scintillator is believed to be strong evidence of d-d fusion reaction. Details on neutron measurement system and the results are given in the previous papers[7,11].

Now we must describe the results with attempting to distingush between the phenomena occurred by cold fusion and those of usual metal hydride system. It is obviously difficult to catch the evidence of d-d fusion except neutron data but comprehensive grasp of the experimental facts leads us understanding the phenomenon.

Dilation of Exp.1

A sample for microscopic observation was removed from the apex of the electrode after interruption of electrolysis and demantling the electrode from the cell. The diameter of the electrode was measured at three positions in height(top, middle and bottom as shown in Fig.2). Then, the electrode was carefully re-installed. Table 1 shows details of the procedures of each run. In Fig.2 the dilation of Pd electrode was plotted against the run number. For 1st run the dilation at bottom end shows the maximum 7 %, while those in the upper regions exhibited the lesser extent than that at bottom. During 2nd~4th run the values at these positions approached asymptotically to 7.8~8.3 %.

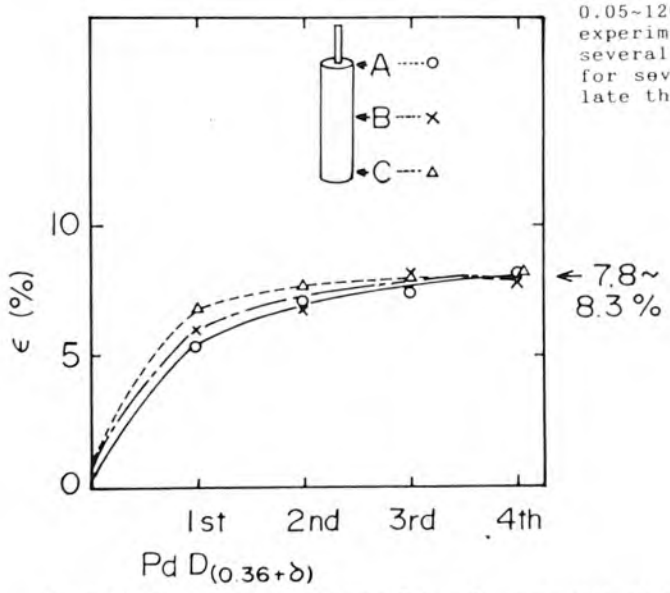


Fig.2 Radial dilation: ε % of post electrolysis Pd electrode at three positions (A, B and C) during 1st run.

It is noted that high CRN and energy spectrum of 2.45 MeV were appeared in the period of 1st run, where the most large dilatation occurred especially during 1st run. Although we have found no explanation about the relation between a neutron emission and large expansion of a material, it is helpful in understanding anormaly to inspect the inside in an aspect of metallography.

The microstructure obtained from the apex is shown in Fig.1 . In metallographic aspect the specimen as a whole is consisted of columnar crystals, which are gradually grown inside from a crucible wall during cooling. The picture of the specimen exhibits a peculiar grain structure, quadrified by two straight grain boundaries. Long prisms grow longitudinally along the electrode center. However, these results are unexpected, since temperatures of the electrode and that out side of the counter electrode showed no significant change corresponding to heat bursts. Hence, this is well acceptable, only when the small heat evolution in the interior lasts long time so as to promote abnormal grain growth. Coupland et al.[14] found the recrystalline grain near the areas of electrical connection. However, there has not been hitherto reported such kind of anomalous grain structure. This suggests that during emission of neutron, the heat evolution in the interior occurred slowly showing the symmetrical crystal structure. However, there is no experimental evidence that relates neutron emission to the increase of temperature assuming such huge heat bursts introduced by F&P.

OP and CRN of Exp.2

The experimental set-up and measurement system were the same as those of Exp.1, whereas twice thicker Pd electrode underwent a deuterium loading during a longer period was used. In spite that the electrode was subjected to high cathodic OP for a long time, the surface sustained the initial metallic gloss. The gloss of the electrode surface in Exp.2 was changed less than that in Exp.1, because the latter electrode had been treated with mechanical abrasion and chemical etching several times. Table 2 shows experimental results for the OP of the Pd electrode, which was deuterium charged galvanostatically. A current density was raised step by step 0.05~120.4 mA/cm^2, then two temperature cycle experiments: 50°C after cooling at 40°C for several hours and 50°C after cooling at 30°C for several hours, were performed to stimulate the transportation of adsorbed deuterium.

Temperature or Current Density Changed at	Current Density (mA/cm^2)	Palladium Overpotential (V)	Temperature of Circulating Water (°C)
1990			
July			
14	0.05	−0.92	40
19	0.10	−0.94	40
26	0.20	−0.99	40
August			
3	0.40	−1.02	40
10	0.80	−1.07 to −1.04[a]	40
17	1.60	−1.12 to −1.08[a]	40
24	3.20	−1.22 to −1.18[a]	40
September			
5	6.40	−1.31	40
10	12.8	−0.72 to −0.68[b]	40
19	25.6	−0.83 to −0.79, −1.44[c]	40
26	51.2	−1.00 to −0.97[b]	40
October			
17	102.4	−2.55	40
25	102.4	−2.44	50
November			
1	102.4	−2.44	50[d]
5	102.4	−2.44	50[d]
11	102.4	−2.44	50[d]
21	102.4	−2.44	50[e]

Table 2 Conditions of electrolysis; [a] Periodically changing, [b] Frequently changing, [c] See text, [d] After cooling at 40°C for several hours, [e] After cooling at 30°C for several hours.

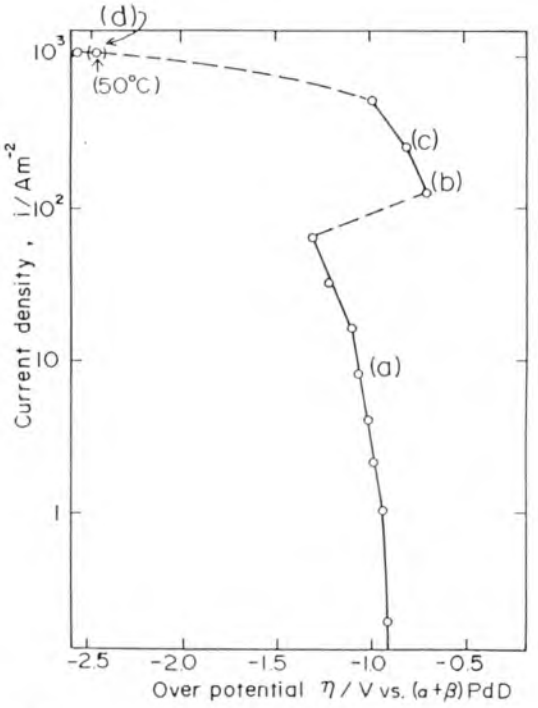


Fig.3 Current-potential curve for pre-loaded Pd in 0.1MLiOD at 40 and 50°C, each point shows a average value during long-term electrolysis, where (a)~(d) indicate the conditions in Table 2.

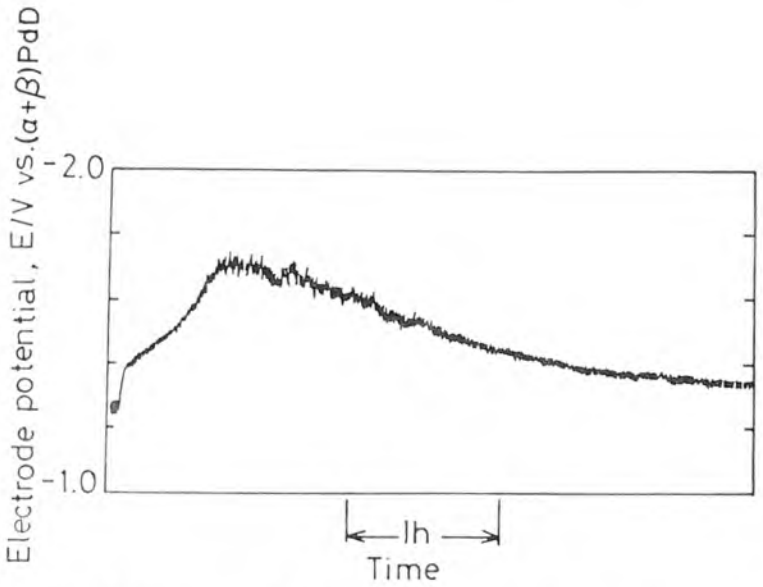


Fig.4 Strange behavior of the overpotential observed at a current density of 51.2 mA/cm^2.

In Fig.3 current-potential curve exhibits the Tafel line with the slope of 0.21 V/decade. The value of the slope is well consistent with that reported by Augustynski et al.[15]. At 102.4 mA/cm^2 the OP rises to almost -2.5 V; (d) in Fig.5, which is associated with poisoning of impurities of the electrolyte such as Zn and Pb or an underpotential deposition of Li^+.

Early state of electrolysis the OP changed periodically for 0.4 to 1.6 mA/cm^2. At 25.6 mA/cm^2 the OP drastically decreased from -1.31 to -0.7 V, then increased to -1.44 V 4 days later and then again decreased to -0.73 V 1day later. Afer then, the OP showed strange behavior, which is shown in Fig.4. Thus, when the current was increased to 25.6 mA/cm^2, the abrupt decrease of the OP (ΔV =0.6 V) was observed as is shown in the transition (a) to (b) in Fig.3. Mengoli et al. reported similar OP shift[16]. This kind of OP shift is far beyond the knowledge of ordinary electrochemical reactions. Hence, the other physical or chemical origin is asked for the strange behavior, which seems to be attributable to surface composition change or possibly heat effect by cold fusion. The latter case is not reasonable for our results because high CRN appeared over -2.55 V at 102.4 mA/cm^2 (refer Fig.5 (d)). This behavior may be explained in terms of an underpotential deposition of Li^+, which increases the OP due to change of surface condition of the cathode. There was no corresponding change of the OP to the high CRN, which may show that the cold fusion does not take place at the surface of the cathode[7].

The neutron measurement was interrupted three times during the long-term electrolysis because the printer brokedown. Since the multichannel analysers (MCAs) malfunctioned during the long time experiment, the foreground results was compared with that of low count rate which was assumed to be equivalent to the background. Figure 5 shows the count rate of neutron (CRN) bunched into 3 h intervals against time. Although during low count rate (Aug.5~Sep.5) no significant energy spectra of neutron was observed, there appeared a difference at 51.2 mA/cm^2. In Fig.5(c) gradual increase and decrease of CRN was appeared apparently coincident to increase of either current density or temperature. Thus, this CRN fluctuation was fairly reproduced in Exp.2. In Fig.5 (d) high CRN, which is three times higher values than that of background CRN bunched into 10 min. appeared a few days after changing the current density or the temperature of the circulating water. Appropriate three energy spectra were averaged during the periods of high CRN observed. The spectrum obtained by substracting the background spectrum (scaled counts per minute) is shown in Fig.6 , together with that of monochoromatic 2.45 MeV neutron (dotted line). The significant signal above the background strongly supports the occurrence of d-d fusion in Pd/D system.

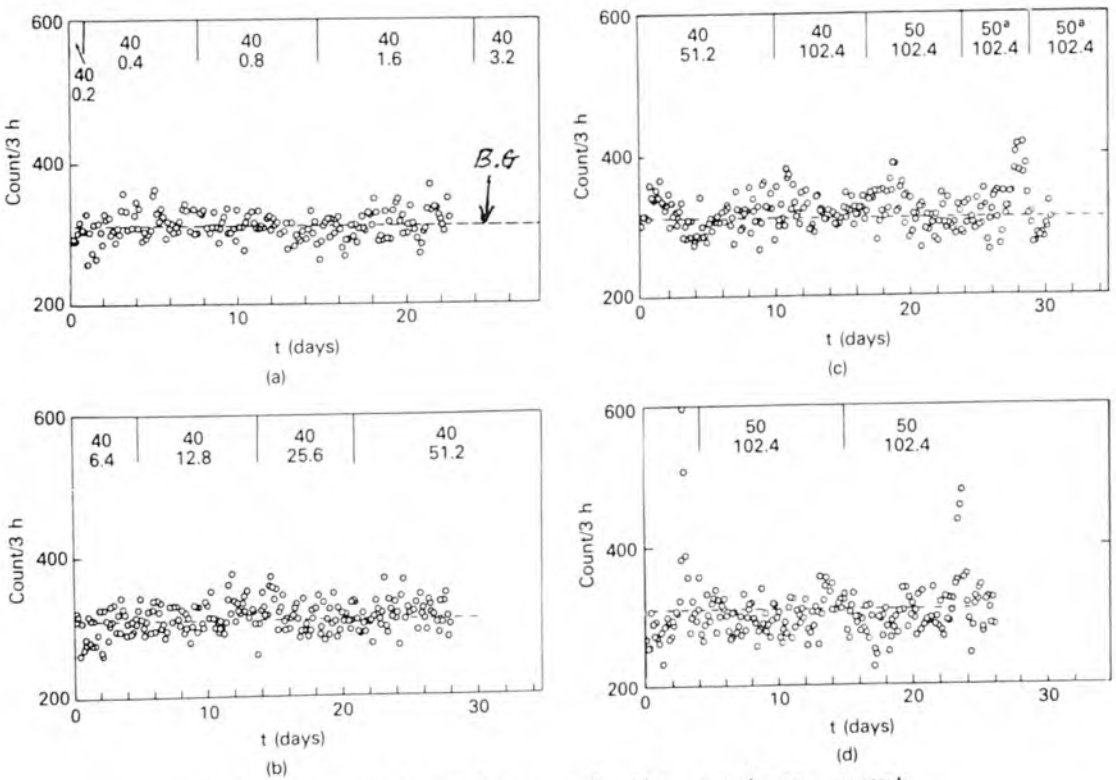


Fig.5 Time dependence of the neutron count rate for 3 h (a) August 2 to August 25, (b) Septenber 5 to Octobcr 3, (c) October 7 to November 7, and (d) November7 to December 3. Upper and lower numerical values in figures mean the temperature of the circulating water in degree Celsius and the current density in mA/cm^2, respectively.

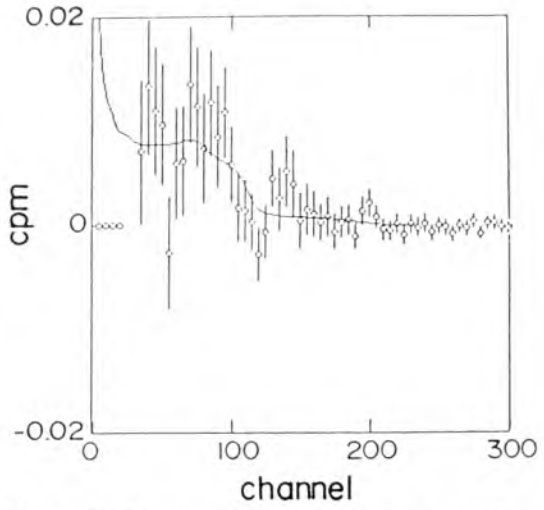


Fig.6 Difference in neutron energy spectrum.

Microscopic mechanism of dilation

Visual observation of the electrode surface is characterized by three different morphology, which is schematically drawn in Fig.7. We found no surface crack, but two faults (Fig.7 (c)), marked blisters (a) and blisters like a feather pattern to arrange each other in two arrays (b). These morphologies locate at 120° left turn and 120° and 150° right turns from the reference position: (b). Thus, there appeared two line imperfections; a long fault and a center line of the feather pattern all over the surface. It is verified that the traverse grain boundary on the crosssectional area of Pd electrode (Fig.12) thrusts out one side at the fault and the other side at the center of the feather. Without chemical etching SEM photographs show partly a plain terrace exposed (Fig.8) , partly covered by a gray overlayer along a long fault. Figure 9 shows another picture of the surface; a cross slip, which is attributable to a heavy local plastic deformation.

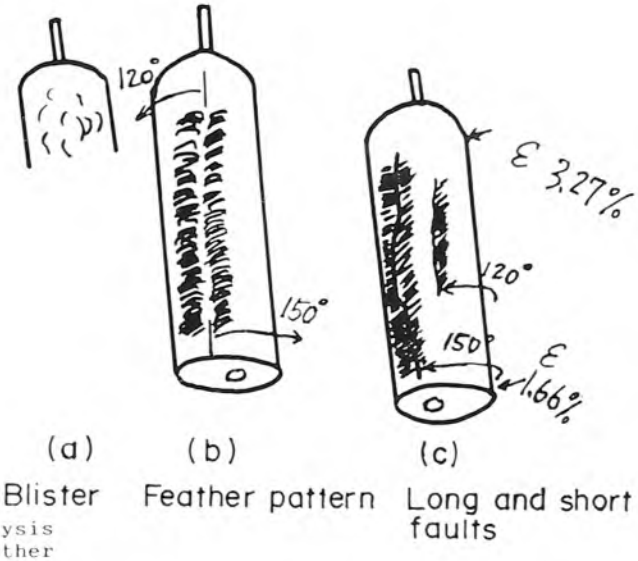


Fig.7 Surface appearance of post electrolysis Pd electrode showing (a) Blister, (b) Feather pattern, center line is reference position, and (c) Two, long and short faults.

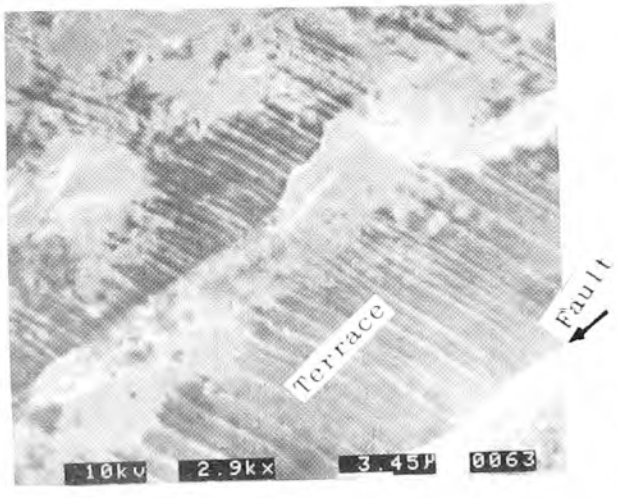


Fig.8 Scanning electron micrograph of Pd electrode surface showing exposed terrace along the long fault.

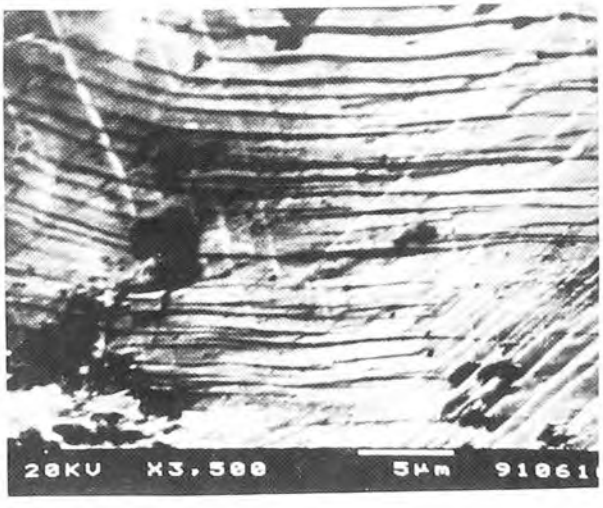


Fig.9 Scanning electron micrograph of Pd electrode surface showing cross slips by local plastic deformation.

On the other hands, the long fault gathers holes. The morphology of holes is shown in Fig.10 . The density of these holes decreased with increasing the distance from the fault line. Figure 11 shows the distribution profile of holes at three positiions (A 6.0, B 3.5, C 8.0 mm apart from the bottom side). Thus, it is considered that both morphologies; faults and holes are relevant. The microstructure of deuterium loaded Pd as a whole shows inhomogeneous structure, the core structure and a blanket as is illustrated in Fig.12 from optical microscopic observation. It consists of two big columnar grains in the interior and columnar grains with randam orientations near the surface. It seems that the latter grain structure was remained unchanged throughout the process, while the core was recrystallized resulting a grain growth. During a long term deuterization, the lattice of big two crystals expands different direction aligned in the figure, which cause a fault and/or a regular arrayed blister on a surface. Then, holes were formed around a fault, whereupon the deuterium gas including the reaction products of the inside gushed. It is useful to compare the formation process of a long fault and blisters with those found in a crater, fault and the behavior of mantle movement inside the earth. The earth evolves heat constantly. In the interior mantle behaves like the mis-oriented Pd grains . Its movement causes a fault and a crater on a crust where a volcano erupts gushing volcano gas, which is consistent with the process of the hole formation around the fault. Thus, several similarities are found between the behavior of deuterium loaded Pd electrode and geological features on the earth. Hence, we can support that the microstructure of Pd electrode is attributable to the heat evolution and plastic deformation in the interior.

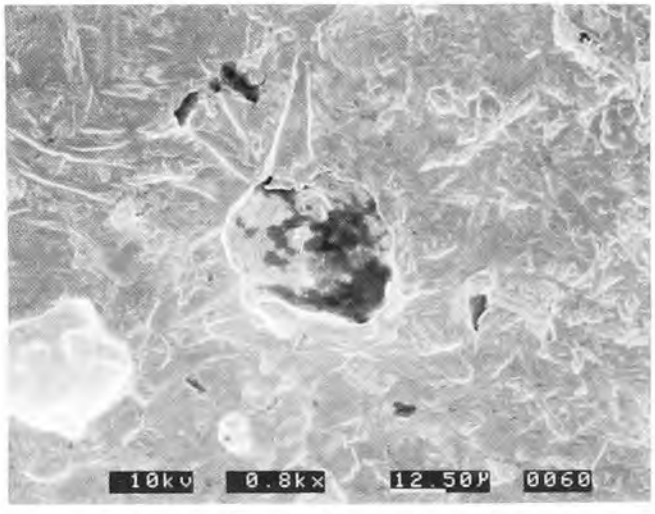


Fig.10 Scanning electron micrograph of Pd electrode surface showing the holes.

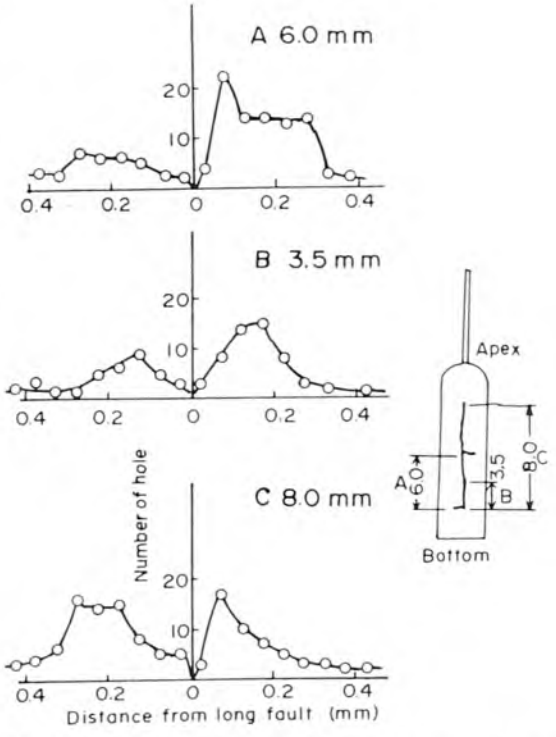


Fig.11 Distribution profile of the holes around the long fault.

Further, the microstructure of crosssectional area of post electrolysis Pd was carefully observed by SEM because it is verified that the neutron emission is not concerned with the surface conditions. As is shown in Fig.12, the interior was composed of two big crystals, one of which had a peculiar morphology; a row of defects. Figure 13 shows the morphology of the defect and their arrangement. Each defect is surrounded by differently colored layer, which seemed to be subjected to the change of physical conditions, i.e. temperature. The inner surface of the defect consists of rounded humps like a nodule. It might be exposed to high temperature and pressure atmosphere.

CONCLUSION

In Exp.1 high CRN was observed during 1st run when large dilation of the cathode occurred at the same time. Metallographic features in the interior show anomalous recrystallized structure, which is attributable to slow heat evolution.

To test reproducibility Exp.2 have been performed using the same set-up, which showed high CRN and neutron energy spectrum of 2.45 MeV. The significant signal above background supports the occurrence of a fusion in Pd/D system. In any experiment the relation of neutron emission to temperature and the OP was not verified.

ACKNOWLEDGEMENTS

The authors wish to acknowledge useful assistance with Mrs. M. Kaneko and K. Hattori. One of authors (H.N.) is grateful to Drs. M. R. Staker and M. Fabrizio for helpful discussions.

REFERENCES

(1) M. Fleischmann and S. Pons; J. Electroanal. Chem., **261**,301 (1989) ; see also Errata; J. Electroanal.Chem.,**263**,187(1989).
(2) S.E. Jones, E.P. Palmer, J.B. Czirr, D.L. Decker, G.L. Jensen, J.M. Thorne, S.F. Taylor and J. Rafelski; Nature,**338**, 737(1989).
(3) H.O. Menlove, M.M. Fowler, E. Garcia, M.C. Miller, M.A. Paciotti, R.R. Ryan and S.E. Jones; Work-shop on Cold Fusion Phenomena May.23-25 (1989),Santa Fe; J. Fusion Energy, 9(4) (1990).
(4) A.De Ninno, A. Frattolillo, G. Lollobattista, L. Martinis, M. Martone, L. Mori, S. Podda, F. Scaramuzzi; Europhysics Letters, **9**,221(1989).
(5) T. Mizuno, T. Akimoto and N. Sato; Denki Kagaku, **57**, 742(1989).
(6) A. Takahashi, T. Takeuchi, T. Iida and M. Watanabe; J. Nucl. Sci. Tech.,**27**, 663(1990).
(7) R. Takagi, H. Numata, I. Ohno, K. Kawamura and S. Haruyama; Fusion Technology,**19**, 2135(1991).
(8) Z. Hongyu et al.; presented at the 2nd Annual Conference on Cold Fusion, Como, 1991.
(9) M. Bittner, A. Meister, D. Seeliger, R. Schwierz and P. Wustner; presented at 2nd Annual Conference on Cold Fusion, Como 1991.
(10) M. McKubre; presented at 2nd Annual Conference on Cold Fusion, Como 1991.
(11) H. Numata, R. Takagi, I. Ohno, K. Kawamura and S. Haruyama; Proc. of the 57th Annual Mtg. of the Electrocem.Soc. Japan, p.30,Kyoto (1990).
(12) Y. Arata and Y.C. Zhang; Kakuyugo-Kenkyu, **62**,398(1989). in Japanese
(13) J. Tafel; Z.Physik.Chem.,**50A**,641(1905).
(14) D.R. Coupland, M.L. Doyle, J.W. Jenkins, J.H.F. Notton, R.J. Potter and D.T. Thompson; Proc. 1st Annual Conference on Cold Fusion, p.299, Utah (1990).
(15) J. Augustynski, M. Ulmann and J. Liu; Chimia, **43**,355(1989).
(16) G. Mengoli, M. Fabrizio, C. Manduchi, L. Riccardi, G. Zannoni, A. Buffa; presented at 2nd Annual Conference on Cold Fusion, Como 1991.

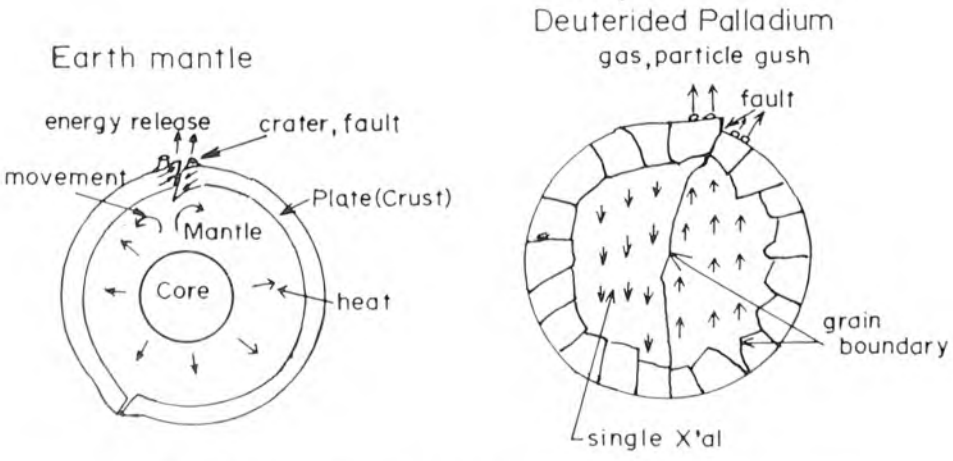
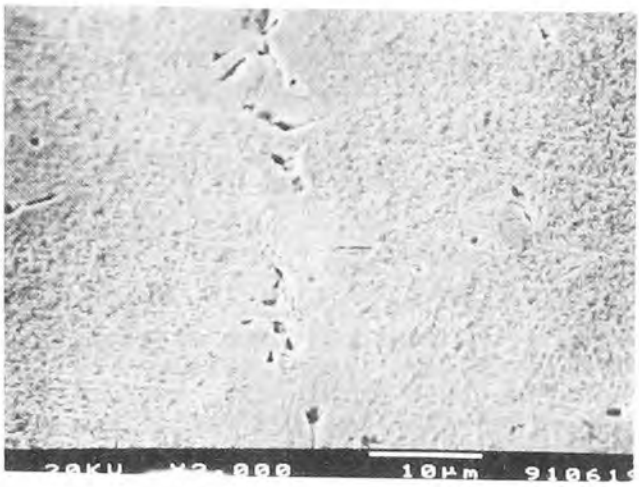
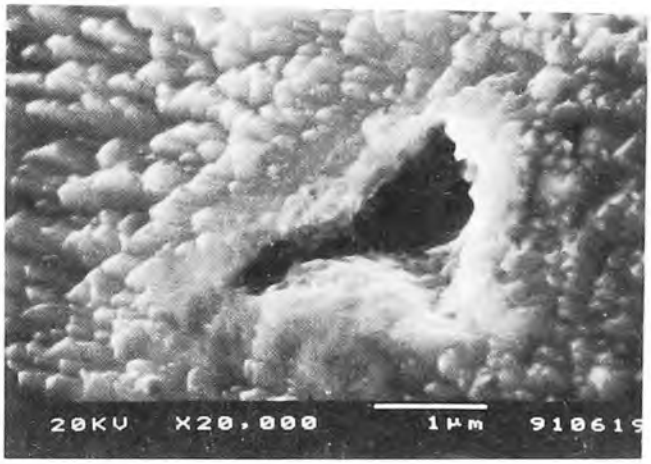


Fig.12 Mechanism of surface faults formed along the fault of Pd rod during a long-term discharging in 0.1 M LiOD.



(a)



(b)

Fig.13 Scanning electron micrograph of cross-sectional area in the midle position of Pd rod, lightly etched. (a) Row of defects (b) Defect

EDITORIAL NOTE TO THE PAPER " NEUTRON EMISSION AND ..."
BY H. NUMATA ET AL.

The decision to publish these Proceedings as soon as possible did not allow any revision of the English presentation of the text originally submitted. This paper contains a few misprints and improprieties, for which we apologize with the readers.