

A Study on Electrolysis of Heavy Water and Interaction of Hydrogen with Lattice Defects in Palladium Electrodes

Won Il Ko* and Young Ku Yoon

Korea Advanced Institute of Science and Technology

Yong Ki Park

Korea Research Institute of Standards and Science

(Received December 13, 1991)

팔라듐전극에서 중수소의 전기분해와 수소와 격자결함의 반응에 관한 연구

고원일* · 윤용구

한국과학기술원

박용기

한국표준과학연구원

(1991. 12. 13접수)

Abstract

Excess tritium analysis was performed to verify whether or not cold fusion occurs during electrolysis of heavy water in the current density range of 83~600 mA/cm² for a period of 24~48 hours with use of palladium electrodes of seven different processing treatments and geometries. The extent of recombination of D₂ and O₂ gases in the electrolytic cell was measured for the calculation of accurate enthalpy values. The behavior and interaction of hydrogen atoms with defects in Pd electrodes were examined using the Sieverts gas charging and the positron annihilation(PA) method.

Slight enrichment of tritium observed was attributed to electrolytic enrichment but not to the formation of a by-product of cold fusion. The extent of recombination of D₂ and O₂ gases was 32%. Hence the excess heat measured during the electrolysis was considered to be due to the exothermic reaction of recombination but not to nuclear fusion.

Lifetime results from the PA measurements on the Pd electrodes indicated that hydrogen atoms could be trapped at dislocations and vacancies in the electrodes and that dislocations were slightly more preferred sites than vacancies. It was also inferred from R parameters that the formation of hydrides was accompanied by generation of mostly dislocations. Doppler broadening results of the Pd electrodes indicated that lattice defect sites where positrons were trapped first increased and then decreased, and this cycle was repeated as electrolysis continued. It can be inferred from PA measurements on the cold-rolled Pd and the isochronally

* 현 한국원자력연구소 근무

annealed Pd hydride specimens that microvoid-type defects existed in the hydrogen-charged electrode specimen.

요 약

상온핵융합의 실험적 검증을 위하여 가공조건 및 기하학적조건이 다른 7종류의 팔라듐전극을 사용하여 24~28시간, 전류밀도 83~600 mA/cm²의 조건하에 전기분해를 실시하였다. 상기조건 하에서 삼중수소의 농축에 기인한 분리팩타(separation factor)를 측정하였고 핵융합의 부산물일 수도 있는 삼중수소 증가량을 측정하였다. 또한 초과열 계산과 관련된 K(net Faradic efficiency)를 측정하여 산소/중수소 가스의 재결합정도를 조사하였다. 양전자소멸측정장치 및 일정체적 가스주입장치를 이용하여 팔라듐전극에서 격자결합과 수소의 반응 및 거동에 대하여 조사하였다.

전기분해하는 동안 삼중수소 농축현상이 관찰되었으나 핵융합의 증거가 될만한 삼중수소량은 검출되지 않았다. 한편 산소/수소 가스의 재결합 정도는 32%로 나타났다. 이는 재결합과정이 발열반응이므로 전기분해과정에서 핵반응과 관계없이 초과엔탈피가 발생할 수 있음을 의미한다. 양전자소멸측정장치를 이용하여 양전자수명, 양전자소멸밀도, P/W 및 R 파라미터의 측정을 통하여 전극의 격자결합(전위 및 공공)에 수소가 집적(trap)되며 수소집적은 공공에서 보다 전위에 약간 더 선호하는 것으로 나타났다. 전극의 수소화물형성에 수반하여 대부분 전위가 발생한 것으로 나타났다. 또한 팔라듐수소화물의 동시소둔실험을 통하여 소량의 미소공동 형태의 결함이 존재하는 것으로 추정하였고 그 결함의 크기는 수 Å정도인 것으로 생각된다.

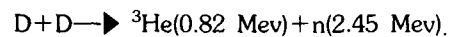
1. Introduction

Recently, many investigators reported the observations of anomalous production of excess heat, neutrons and tritium during constant current electrolysis of heavy water with use of the palladium electrode.[1~3] If these phenomena proved to be true, it could have significant impact on development of a new energy source. There are some unanswered questions, however. The fusion by-products were observable only in sporadic bursts, and no reproducible results could be obtained. Experimental results reported so far were not all convincing because the tritium enrichment by isotope effects during electrolysis and the effects on measurements of excess heat due to the recombination of O₂ and D₂ were not fully taken into account. Nevertheless, Srinivasan [3] reported the production of tritium at levels of ~10² to ~10⁴ times its background levels in a few cells. This result cannot be readily explained as the effect of isotope enrichment. The dominant chan-

nels for D-D fusion are



and



Therefore, the observation of neutrons and tritiums is very important to confirm nuclear fusion. The detection of neutrons, however, is more difficult than that of tritium and it requires more elaborate measurement because of its very low emission rate generally. The purpose of the first phase of this study was to verify cold fusion phenomena by investigating whether excess tritium is emitted during electrolysis of heavy water at the palladium electrode and effects on measurements of excess heat due to the recombination of D₂ and O₂. The tritium enrichment and possibility of emission of excess tritium by electrolysis were examined with use of the liquid scintillation counter (LSC). The extent of recombination of D₂ and O₂ in the electrolytic cell was measured for the cal-

ulation of accurate enthalpy values.

Since the calculated fusion rate at the internuclear separation of 0.74 Å in the deuterium molecule is $\sim 10^{-64}\text{S}^{-1}$ [4], and the known interstitial site separation is approximately 3Å, the rate reported by Jones[2], namely, 10^{-23}S^{-1} cannot be explained. Hence if the fusion reaction in the palladium lattice really occurred, it could be assumed that the nuclear fusion reaction occurs due to an effect of lattice defects or an unknown mechanism for non-equilibrium state during electrolysis. The following different models or mechanisms that may possibly explain the cold fusion experiments have been suggested since these can not be simply interpreted by today's existing nuclear physics. : piezonuclear fusion[2] due to the formation of ultra-high pressure in voids in the palladium lattice, crack induced fusion[4] by acceleration of deuterium ions due to the high voltage drop across fine cracks as cracks grow instantly, muon catalyzed fusion[5], and surface model[6] due to the formation of dendrites during prolonged electrolysis on the electrode surface. In the light of the above discussion, it is necessary for better understanding of cold fusion mechanisms to examine the behavior and interaction with defects of hydrogen that behaves similarly as deuterium in palladium electrodes. To examine the effects of hydrogen charging of palladium electrodes and the interaction of hydrogen atoms with lattice defects, the following studies were conducted with use of the positron annihilation(PA) technique and Sieverts gas charging method : New defects occurring during hydrogen charging were examined by PA measurements on cold-rolled Pd and the Pd hydride specimen. The interaction of hydrogen atoms with lattice defects in none-equilibrium state during electrolysis was then inferred from Doppler broadening measurement. The preferred defects sites for hydrogen trapping were also examined from PA measurements of trap-intensities.

II . Positron Annihilation Measurements

II-9. Principles

When positrons with certain energy enter the condensed matter, they lose their energy within a few psec by ionizing collisions, positron-electron inelastic scattering and phonon scattering. This process is known as thermalization. The implantation depth of positrons in metals is dependent upon the positron source and metal density. It is usual 100~200 μm in metals for positrons from ^{22}Na that is the most commonly used isotope. [7] The probability of finding a positron in the perfect lattice is highest at the interstitial sites and lowest at the sites of ion cores of metal because a positively charged positron is repelled from the ion core with the same charge. A thermalized positron annihilates through the recombination with an electron and emits two gamma quanta of mainly 511 keV.

The decay scheme of ^{22}Na and the basic principles of three types of positron annihilation measurement, namely, that of lifetime, Doppler broadening and angular correlation are illustrated in Fig. 1. The ^{22}Na decay emits positrons and characteristic γ -rays within a few psec. Hence the life time of the positron can be detected by measuring the time gap between the births of the initial γ -ray of 1.274 MeV and the annihilating γ -ray of 511 keV. The average lifetime of positrons and the Doppler broadening parameters are characteristic of particular materials and their defect conditions. Details of positron annihilation measurements and their interpretation are reported elsewhere. [8].

II-2. Positron Annihilation in Defected Metals

If there are defects in metals such as vacancies or dislocations, positrons are trapped and the life-

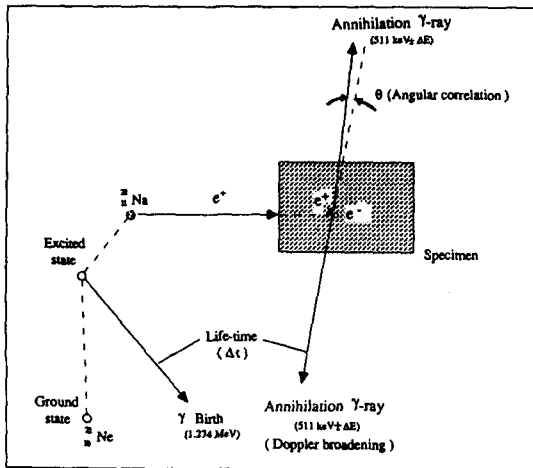


Fig. 1. The decay scheme of ^{22}Na and illustration of three parameters (lifetime, Doppler broadening, angular correlation) of positron annihilation measurements

time becomes longer since the electron density at such defects is lower than at a regular lattice site. Since each type of defects has a distinct electron density profile, positron life time is different for different type of defects in a given material. Hence positron life time can be a fingerprint of each type of defects.

Difference in the electron density profile around defects also affects the Doppler broadening energy spectrum of annihilating γ -rays. In metals a positron annihilates not only with a valence electron but also with a core electron. Because of the higher momentum of a core electron, the Doppler shift of an annihilating γ -ray emitted from a positron-core electron pair is higher than that from a positron-valence electron pair. Since the density of core electrons is diminished, Doppler broadening line-shape becomes narrower and sharper when a positron interacts with a defect. Details of Doppler broadening line-shape parameters (D , W , R) and their analysis methods have been reported elsewhere. [8].

I-3. Positron Annihilation in Metal-Hydrogen System

The possibility of utilizing the positron annihilation technique in studies of hydrogen trapping and embrittlement of metals has been investigated on the basis of the following physical processes. Hydrogen atoms dissolved in a metal exist in the form of protons and electrons, and these enter the conduction band of the host metal. [9] Since positrons have the same charge, and they are also apt to be trapped at the same type of defects, the positron trapping capability of each type of defects in a metal-hydrogen system is reduced because of proton repulsion. Hence if the positron lifetime and other parameters are measured for a metal before and after hydrogen is charged into the metal, it is possible to find actual hydrogen trapping sites and the frequency of hydrogen trapping.

I-4. Hydrogen in Palladium Crystal

The palladium-hydrogen system has been studied for many years because of the widespread use of palladium as a hydrogen purifier and a membrane that permits a rapid rate of permeation of hydrogen. In the low hydrogen content region of primary solubility its solubility is described by the Sieverts law as $n = K_s P^{1/2}$ where n is the atom ratio of H to Pd. As the hydrogen concentration increases, deviation from the Sieverts law due to H-H attractive interaction occurs. This interaction ultimately leads to the formation of the second hydride phase (β -phase). In the regions of primary solubility where both the α -phase and the β -phase exist, absorbed hydrogen atoms have been shown to occupy octahedral interstitial sites. [10] Since the formation of hydrides results in an abrupt expansion of the lattice from $a_0 = 3.985 \text{ \AA}$ (α -phase) to 4.025 \AA (β -phase) at 24°C , the stress fields are created. [11]

It also has been shown that there is a significant solubility enhancement of hydrogen in the region of the α -phase in cold worked palladium.[12] This increased solubility is attributed to trapping of hydrogen atoms in the strain fields of dislocations. The role of vacancies in hydrogen trapping has not been verified experimentally, however, because the size of vacancies is very small and its control is difficult. If the PA instrument that can distinguish a unit vacancy is used, the possibility of hydrogen trapping at a vacancy can be determined indirectly.

Following the transformation of the α to the β -phase, the solubility of hydrogen under a given equilibrium pressure is enhanced. The currently favored explanation for this is that hydrogen is trapped at dislocations generated during the phase change since there are marked similarities between the hydrogen absorption isotherm following the phase change and that exhibited by heavily cold worked palladium.[13].

II. Experimental Methods

II-1 Electrolysis

II-1.1 Tritium Measurements

Tritium that occurs as a by-product of cold fusion appears to be the least ambiguous evidence and also is the most easily measured. The production of tritium can be possible due to not only fusion reaction but also to enrichment during electrolysis. A build-up of tritium in the electrolytic solution without fusion can occur because deuterium is evolved preferentially over tritium when heavy water is electrolyzed. The tritium enrichment can be expressed as: [14]

$$V_f/V_o = [N_f/N_o]^B \tag{1}$$

where N_o and N_f are the initial and final numbers

of tritium atoms in the electrolyte, B is the isotopic separation factor that usually ranges from 1.6 to 2, and V_o and V_f are the initial and final volumes of the electrolyte.

The electrolytic cell used in the present study is shown in Fig. 2a. The anode used in the cell was the same for all experiments, namely, a 1mm diameter platinum wire, and heavy water containing 0.1 M LiOD was used for electrolysis. The electrolytic solution was prepared by dissolving metallic lithium of 99 % purity in heavy water of 99.75 % purity. Table 1 summarizes the heat treatment conditions, geometry and dimensions of the electrode specimens.

Electrolyses were conducted with the current density range of 83~600 mA/cm² for a period of 24~48 hours. Experimental conditions are

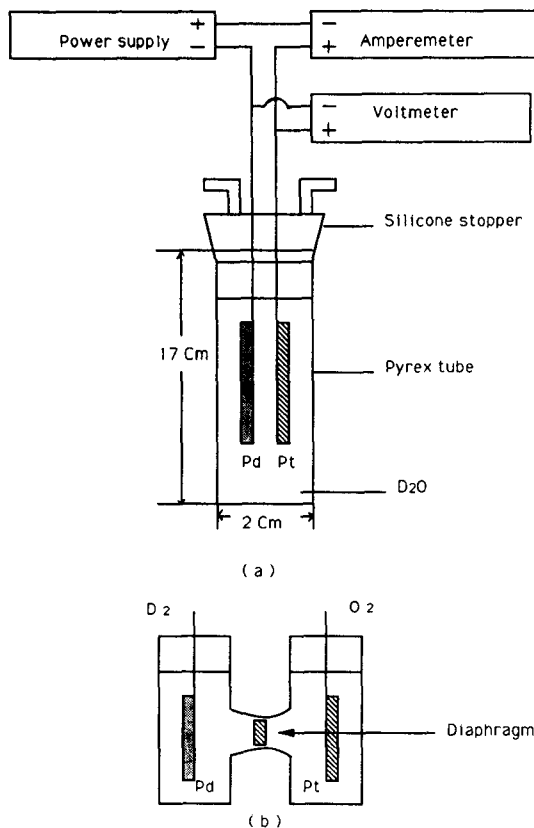


Fig. 2. Schematic diagram for measurement of D₂-O₂ recombination

Table 1. Various processing and geometry conditions of the palladium electrode specimens

Specimen	Processing conditions	Geometry	Dimensions unit : cm
S1	as 50% cold rolled	sheet	5.6×0.13×0.25
S2	as annealed for 24 hrs at 1100°C in vacuum	rod	0.2D*×5
S3	as extruded	rod 0.2D×5	
S4	as cast	irregular** lump	
S5	as quenched to 0 °C after annealing at 1100°C	sheet	5.3×0.2×0.2
S6	as annealed for 24hrs at 1100°C in vacuum	sheet	5.0×0.24×0.13
S7	as extruded and given D ₂ gas charging (1 atm) for 2 hrs at 150 °C	rod	0.1×5

* D denotes diameter

** small broken pieces of cast palladium with irregular surface and geometry

summarized in Table 2. Beta particles arising from tritium decay were monitored by the liquid scintillation counter (Beckman model LS 3801). Electrolyte samples of 2.5 ml were taken from the cell and the Aqualuma scintillation cocktail was added to them. They were then allowed to decay for 30 min. to minimize chemiluminescence.

In order to obtain separation factors the palladium cathode was replaced by platinum and values of N_f , N_o , V_o and V_f were then measured. N_f and N_o values were obtained using LSC. Amounts of excess beta particles were recalculated using the equation (1).

1.2 Recombination of D₂ and O₂ Gases

Recombination of D₂ and O₂ gases must be considered to obtain a more accurate enthalpy value for the electrolysis reaction in an open calorimetric system. If the net Faradaic efficiency K of gas evolution is known, the electrolysis power P_{app} then becomes

$$P_{app} = E_{app} \times I = P_{cell} + P_{gas}$$

$$= \{ (E_{app} - K \times 1.54V) \times I \} + K \{ 1.54V \times I \}$$

where P_{gas} represents the power consumed for the evolution of D₂ and O₂ gases, and P_{cell} is the remaining power consumed in heating the cell content. If no gas escapes from the cell due to efficient recombination process, then $K=0$, and

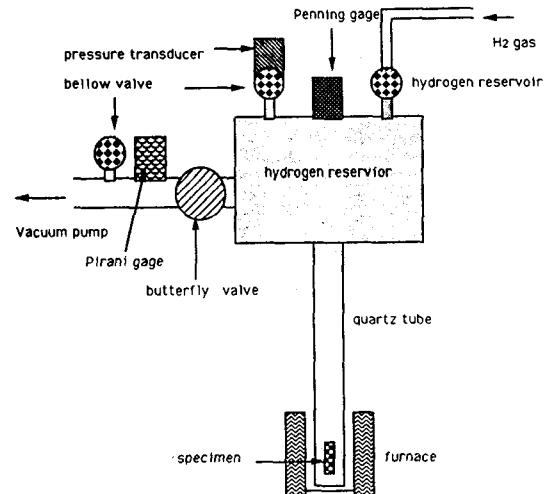


Fig. 3. Schematic diagram of the Sieverts charging system

Table 2. Experimental conditions for measurement of excess radiation

Experiment designation	Specimen	Current density (mA/cm ²)	Charging time(hrs)
E1	S1	83	25
E2	S2	542	25
E3	S3	500	25
E4	S4	600	24
E5	S5	500	24
E6	S1	327	48
E7	S6	486	48
E8	S7	600	24

the above equation results in $P_{app} = P_{cell}$ as expected, with all of the applied power consumed in heating of the cell content. Alternatively, if the gases escape with unit efficiency, then $K=1$, and $P_{cell} = (E_{app} - 1.54V) \times I$. Several investigations [1, 3] have assumed $K=1$ in analysis of the calorimetry data.

The extent of recombination of D_2/O_2 gases was investigated in the present study with use of the two cells each with and without a diaphragm as illustrated in Fig. 2a and Fig. 2b. The extent of recombination was calculated from the measurements of the decrease in the weights of the two cells before and after electrolysis with use of the 40 ml electrolyte at 1018 mA/cm² for 24 hours. The decrease in the weights was measured with use of the Mettler balance (model PC 440 with an accuracy of 0.1 mg), and then the value of K was calculated.

III-2. Positron Annihilation (PA) Measurements

III-2.1 Specimen Preparation

Annealed palladium sheet specimens were cold rolled with reductions of 30, 50 and 70% in thickness to examine effects of dislocations. Specimens

were also prepared by quenching into ice water after the annealing to examine effects of vacancies on positron annihilation measurements. All of the specimens were cut into 2mm×2mm×1mm pieces with use of a diamond wheel cutter and these were then polished on 600 grid paper.

Reference specimens for PA studies were annealed at 1000 °C for 8 hours and were used to calibrate lifetime and Doppler broadening parameters.

Palladium hydrides (PdH_{0.6}) were prepared with use of the Sieverts gas charging system to study what new defects other than dislocations occur due to the formation of hydrides. The palladium hydride specimens were also given isochronal heat-treatments for 2 hours at 100, 200, 300, 400, 500 and 600 °C, respectively. Fig.2 shows the Sieverts gas charging system used.

The lifetime and Doppler broadening parameters were measured with use of the PA measuring instrument in the Non-Destructive Test Laboratory of the Korea Research Institute of Standards and Science. The details of the PA measurement system have been reported elsewhere. [8]

III-2.2. Experimental Methods

PA measurements were made with use of well annealed Pd polycrystalline specimens to determine their positron lifetimes and Doppler broadening line-shapes. These measurements were used as references in analysis of PA measurements data of the above-mentioned specimens. PA measurements were made on several specimens for each specimen processing condition. The average life time and Doppler broadening parameters were obtained from these measurements on 30, 50 and 70% cold rolled specimens and annealed-quenched specimens. Using the above results, the life time at disloca-

tions and vacancies were calculated.

The ^{22}Na isotope of 10 μCi adhered to Kepton foil was used as the positron source. After source life time was determined by analysis of one lifetime component, analyses were performed either by the one or two trap component method.

The variation of the positron trap intensity was measured for 50% cold rolled electrodes that were hydrogen charged in the 0.1 M LiOH water solution at 600 mA/cm² for 10 minutes. These measurements were compared with those for annealed-quenched specimens to examine preferred trap sites of hydrogen atoms.

Well annealed and quenched, and cold rolled specimens were also prepared to examine effects of lattice defects on hydrogen solubility in palladium. Experiments for this study were conducted with the Sieverts gas charging system. The equilibrium pressure at 50 °C was obtained from the pressure drop that could be measured with use of a pressure transducer of the system. The hydrogen solubility was calculated using the ideal gas law ($PV=nRT$). Possibilities of hydrogen trapping at dislocations and vacancies were examined from the solubility results, and these results were compared with results obtained with use of PA measurements.

Doppler broadening line-shape parameters were measured as a function of hydrogen charging time to study the behavior of defects in non-equilibrium state. These measurements were conducted with annealed specimens that were hydrogen charged at 50 mA/cm² for a time interval from 20 to 200 minutes.

The Doppler broadening parameters and its R^* parameters were measured as a function of hydrogen solubility to estimate the solubility limit of

α -phase(α_{max}) and new defects occurring due to the formation of hydrides.

To examine the formation of new defects other than point and line defects occurring due to hydrogen charging, the lifetime and Doppler broadening parameters were measured on PdH_{0.6} specimens prepared with use of the Sieverts gas charging system (Fig. 3).

IV. Experimental Results and Discussion

IV-1. Tritium Measurements

Heavy water used in electrolyses had a tritium content of $0.899 + 0.013 \mu\text{Ci/ml}$ before electrolysis. The tritium concentration measured was increased 21% on the average during palladium cathodic charging. When heavy water of 40 ml was electrolyzed to a final volume of 32.5 ml with use of the platinum cathode to determine tritium enrichment during electrolysis, the tritium concentration measured was increased from 0.896 to 1.071 $\mu\text{Ci/ml}$. Hence the tritium enrichment was observed to occur during electrolysis with use of the cell (Fig. 2 a). It appears from Eq. (1) that the separation factor (B) is 1.62 that is nearly identical to the result reported in Ref. 15, namely, 1.68. The increased tritium concentrations during palladium cathodic charging, 21% on the the average, was recalibrated with this separation factor. The results are shown in Fig. 4. The recalibrated values differ from the average values measured by only about $\pm 8\%$. Hence the observed increase in the tritium concentration can be accounted for by the isotopic enrichment that occurs during electrolysis of heavy water. Under the present experimental conditions, therefore, cold fusion phenomena did not seem to occur since there was no indication of significant tritium production during the electrolysis.

$$* R = |(P_f - P_t) / (W_f - W_t)|$$

where P_f and P_t are the characteristic values of the lineshape parameter for the free and trapped states, respectively. The R parameter is independent of concentration and characterizes the type of trapping centers[8].

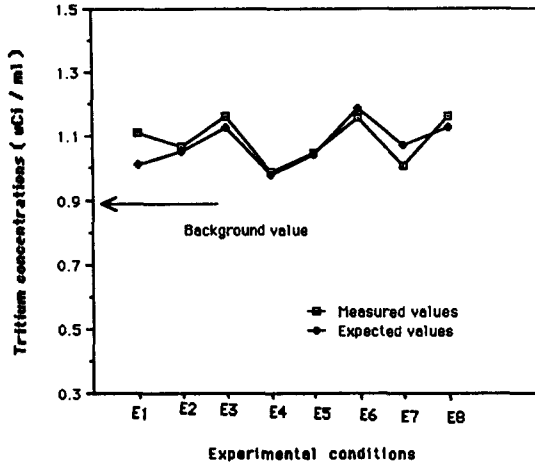


Fig. 4. Beta particle measurements during electrolysis of D₂O with various palladium electrodes

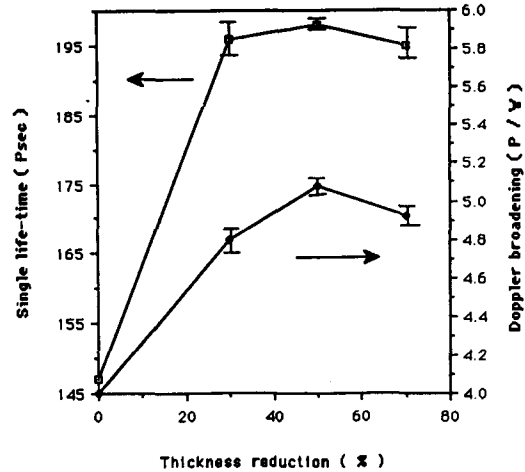


Fig. 5. Variation of the single lifetime and Doppler broadening parameter for cold rolled Pd electrodes

N-2. Recombination of O₂ and D₂ Gases

The mass variation of the electrolytes was measured for the two cells as shown in Fig. 2 before and after electrolysis was conducted under the same conditions of current density and charging time. The mass variation was 0.698 g in the cell as shown in Fig. 2b without recombination of D₂ and O₂ gases, and 0.475 g in the cell as shown in Fig. 2 a. Hence K=0.68, and the extent of recombination of D₂ and O₂ gases in the cell shown in Fig. 2 a is 32 %. This result indicates that the excess heat can be accounted for by exothermic heat of recombination and not by nuclear fusion.

N-3. Positron Annihilation Measurements

Fig. 5 shows the variations of the positron lifetime and Doppler broadening line-shape factor (P/W) as a function of the thickness reduction of the cold-rolled electrode specimens. The lifetime spectra were analyzed in terms of a single lifetime component. The lifetime increased rapidly with increasing reduction to about 30 %. It seems that at this stage positrons are mainly trapped at dis-

locations in cold-rolled palladium electrodes, and the dislocation density increased rapidly as the cold reduction increased up to 30 %. When cold reduction was greater than 50 %, the lifetime and Doppler broadening line-shape factor decreased slightly. The decrease of lifetime and Doppler broadening parameters can be explained as follows; At cold reduction of greater than 50 %, partial cell structure due to the formation of tangled dislocations occurs, and the regions of low dislocation density exist among the regions of high dislocation density. This observation is in good agreement with the result of Jamieson's [16] TEM study of the deformed palladium.

Calibration experiments with palladium electrodes yielded the following results. This positron lifetime of the well annealed palladium was 147 ± 2.8 psec, and the lifetime of the source itself was 427 ± 9.2 psec. The positron lifetime for the dislocations and vacancies in cold rolled and quenched palladium specimens was found to be 184 psec and 189 psec, respectively. It indicates that the size of the edge dislocation core is slightly larger than that of vacancy.

Fractional intensities of positron annihilation at

dislocations and vacancies were reduced by hydrogen charging. The intensity reduction was about 21 % for the cold rolled specimen and 6 % for the quenched specimen. This result indicates that hydrogen occupancy at dislocations and vacancies was about 0.21 and 0.16, respectively, in the cathodically charged specimens. Hence it appears that hydrogen trapping at dislocations is slightly more preferred than at vacancies.

The results of hydrogen solubility measurements in different palladium specimens using the Sieverts gas charging system are shown in Fig. 6. The enhancement of hydrogen solubility was observed for cold rolled and quenched specimens having low hydrogen content (α -phase). The solubility enhancement (n'/n) was 1.42 in the cold rolled specimen and 1.1 in the quenched specimen, respectively, where n and n' are the solubility of well annealed and processed specimen, respectively. It seems that the stress field around the dislocation array gave rise to the solubility enhancement. This result is similar to those for the fractional intensities measurement by the PA method, and is in good agreement with those of other studies for cold rolled specimens.[12] The hydrogen trapping inferred at palladium atom vacancies, however, differs from the result of Fla-

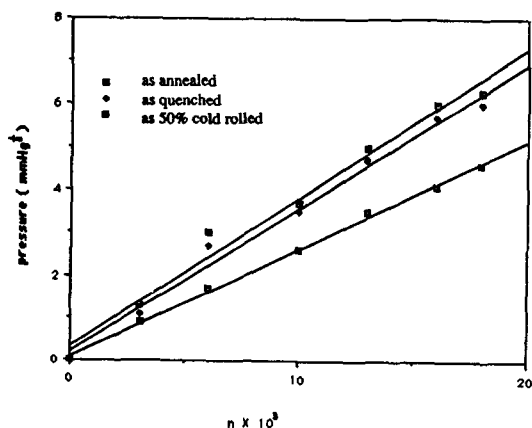


Fig. 6. Plot of equilibrium hydrogen contents vs. the square root of hydrogen pressure at 323 K

nagan[12] that was negative in the hydrogen solubility experiment with quenched palladium specimens. Non-equilibrium vacancies can not be annihilated at room temperature during PA measurements since the activation energy of palladium atom vacancies (1.5 eV) is relatively higher than that of other metals.[12] Hence it allows for the possibility of examining the role of vacancies as hydrogen trapping sites.

The Doppler broadening measurements for the annealed specimens with various durations of hydrogen charging are shown in Fig. 7. P/W line-shape factors increased and then decreased, and this repeated as electrolysis continued. A similar phenomenon was observed with PA measurements for nickel specimens by Byrne.[7] The increase in P/W (region 1, 3) could result from the formation of new defects, and the decrease in P/W following a maximum (region 2,4) could be accounted for by proton screening of the defects. According to Byrne, the reason for the repetitious increase and decrease phenomena may be explained by the fact that newly generated dislocations are less likely to become saturated with protons than those dislocations initially present.

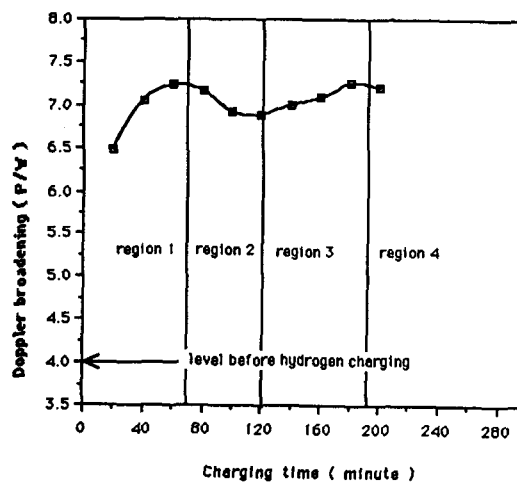


Fig. 7. Variation of the Doppler broadening parameters during electrochemical hydrogen charging as a function of time

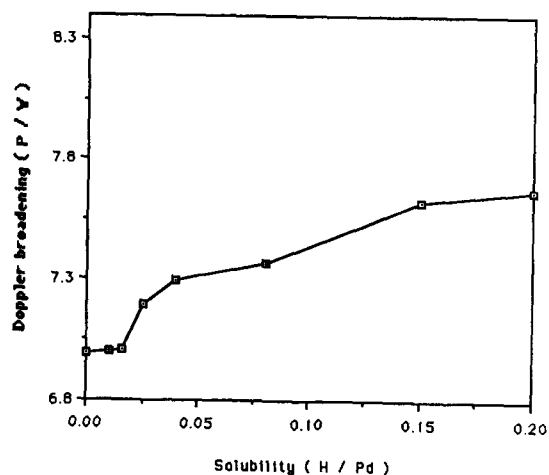


Fig. 8. Variation of the Doppler broadening parameters vs. hydrogen solubility

Fig. 8 shows the results of Doppler broadening (P/W) as a function of hydrogen solubility. It appears that P/W parameters hardly change until the solubility reaches 0.02, and then gradually increase. It indicates that the solubility limit of the α -phase (α_{max}) at 50°C is 0.02. This result is in agreement with that reported in Ref. 15 and 17. The reason for the increase of P/W parameters from the values for PdH_{0.02} can be explained by the creation of new defects due to the formation of the hydride phase. The R parameter calculated from the above results is shown in Fig. 9. Here the increase of the R parameter from the value for PdH_{0.02} indicates that the character of dominant trapping sites change. The R parameter of 1.72 agrees well with the characteristic value of dislocations. It indicates that mostly dislocations are formed as a phase change occurs.

The results of Doppler broadening for the cold rolled palladium electrode and cold rolled palladium hydride (PdH_{0.6}) isochronally annealed are shown in Fig. 10. Since the results of lifetime measurements can not be analyzed because of complication of lifetime analysis for hydride specimens, the specimens were annealed to detrap hydrogen atoms. As shown in Fig. 10, there is

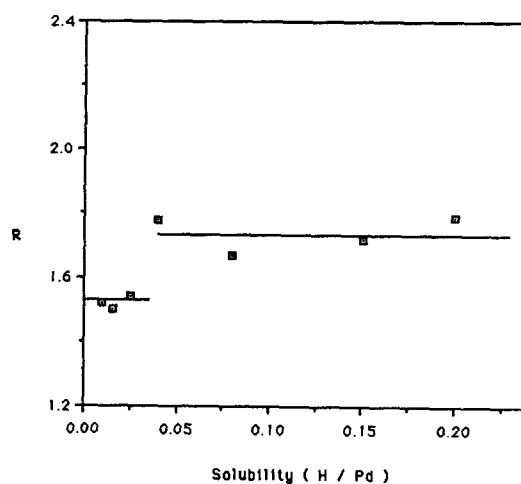


Fig. 9. Variation of the R parameter vs. hydrogen solubility

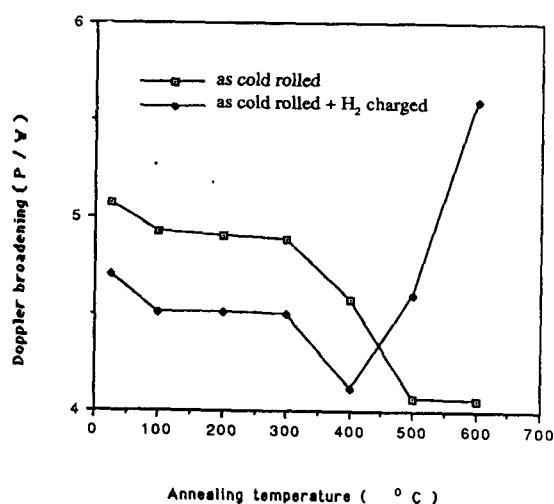
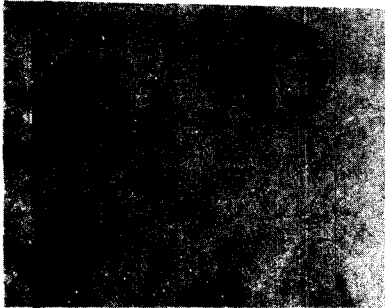


Fig. 10. Variation of the Doppler broadening parameters for cold rolled Pd and cold rolled PdH_{0.6} after isochronally annealing

difference in the cases of the two treatments. The P/W for Pd hydrides (PdH_{0.6}) is smaller than that for the cold rolled Pd until the annealing temperature was increased to 450°C. It could be explained by trapping of hydrogen atoms at defects. The increase of P/W for the PdH_{0.6} in the range of 400~600 °C seems to indicate that hydrogen atoms detrap at defects. The decrease of P/W for the cold rolled Pd in the range of 300~500 °C



(a)



(b)



(c)

Fig. 11. Optical micrographs ($\times 1000$) of palladium electrode specimens of (a) 50 % cold rolled, (b) annealed and (c) annealed and then hydrogen charged (etchant : solution of 25 ml HCl, 5ml HNO₃ and 30ml H₂O)

can be explained by recovery of vacancies and dislocations. It could be inferred that void-like defects existed in PdH_{0.6} because they were not recovered at 600 °C. This result is similar to those reported by Sneed.[18] Lifetimes for the cold rolled Pd specimen and PdH_{0.6} isochronally annealed at 600 °C were analyzed using the two trap component method to estimate the size of void-like defects. It was found that void-like defects with the lifetime of 368 ± 68 psec and intensity of 11% existed in hydrogen charged specimens. By comparison of lifetime measurements for other metals,[19] it can be inferred that the size of the void-like defects is about a few Angstrom(Å).

Fig. 11 shows the optical micrographs of palladium electrode specimens as 50% cold-rolled, annealed, and hydrogen-charged after annealing. In the case of the cold rolled specimen, the grain interior was severely etched due to the existence of high dislocation density. The microstructure of an annealed and hydrogen charged specimen was similar to that of the cold rolled specimen. Hence it can be inferred that cathodic hydrogen charging generates mostly dislocations in the microstructure. This is also supported by the R parameter result obtained from the PA measurement shown in Fig. 9.

VI. Conclusions

Analyses of excess tritium and excess heat production were performed to verify whether or not cold fusion occurs during electrolysis of heavy water in the current density range of 83~600 mA/cm² for a period of 24~48 hours with use of palladium electrodes of 7 different processing treatments and geometries. Interaction of hydrogen atoms with defects in Pd electrodes were examined using the Sieverts gas charging and the positron annihilation (PA) method. The results

obtained from the present study are summarized as follows :

1. Excess tritium that could be considered as a by-product of cold fusion was not detected during electrolysis of heavy water containing 0.1M LiOD in the current density range of 83 ~600 mA/cm² for a period of 24~48 hours.
2. Tritium enrichment that is attributed to the differences in absorption heat and diffusivity of hydrogen isotopes was observed during electrolysis, and its separation factor was determined as 1.62.
3. The measurements of net Faradaic efficiency K indicated that recombination of deuterium and oxygen gases must be taken into account in the measurement of excess heat production during electrolysis.
4. It can be inferred from lifetime results from the PA measurement on the Pd electrode specimens that hydrogen atoms could be trapped at dislocations and at vacancies in the electrodes and that dislocations were slightly more preferred sites than vacancies for trapping hydrogen atoms.
5. Doppler broadening results from the PA measurement on the Pd electrode specimen indicated that the number of lattice defect sites where positrons were trapped first increased and then decreased, and this cycle was repeated as electrolysis continues.
6. It can be inferred from R parameter results from the PA measurement that the formation of hydrides was accompanied by generation of mostly dislocations.
7. PA measurements of the cold-rolled Pd and the Pd hydride specimens annealed isochronally indicated that microvoid-type defects existed in the hydrogen-charged electrode.

References

- [1] M.Fleishmenn and S.Pons. *J.Electroanal. Chem.*, **216**, 301(1989)
- [2] S.E. Jones et al., *Nature*, **338**, 737 (1989)
- [3] M.Srinivasan and P.K. Iyengar, *Fusion Technology*, **18**, 34 (1990)
- [4] J.W. Schultze and U.König, *Electrochimica Acta*, **34**, 1289 (1989)
- [5] Y.D. Yad, C.W. Wang and E.K. Lin, *J. of Materials Science Letters*, **9**, 228 (1990)
- [6] M.P. Soriaga, T. Mebrahtu et al., *J. Electroanal. Chem.*, **267**, 3515 (1989)
- [7] R.M. Nieminen and M.J. Manninen, "Positrons in Imperfect Solids", Positrons in Solid, ed. P. Hautojärvo. Springer-Verlag 145 (1979)
- [8] Seong Je-Garl, Young Ku Yoon and Yong Ki Park, *J. Korea Nuclear Society*, **23**, No 1, (1991)
- [9] S. Mantle and R.M. Singru, *Physical Review B*, **19**, 1391 (1979)
- [10] K. Sköld and G.Nelin, *J. Phys. Chem. Solids*, **28**, 2369 (1967)
- [11] T. Flanagan and J.D. Clewley, *J. Less Common Metals*, **41**, 343 (1975)
- [12] T. Flanagan et al., *J. Less Common Metals*, **49**, 13 (1976)
- [13] J.F. Lynch, J.D. Clewley and T. Curran, *J. Less Common Metals*, **55**, 153 (1977)
- [14] R.A. Allen, D.B. Smith and R.L. Oflet, *Nucl. Instruments Methods*, **45**, 61 (1966)
- [15] H. Wiesmann, *Fusion Technology*, **17**, 350 (1990)
- [16] H.C. Jamison, G.C. Weatherley et al., *J. Less Common Metals*, **50**, 85 (1976)
- [17] R.W. Ure and J.G. Byrne, *Philos. Mag. A*, **39**, 517 (1979)
- [18] C.L. Sneed and K.G. Lynn, "Positron Annihilation" North Holland Publishing Company, 483 (1982)
- [19] M. Doyma, K. Hinode and S. Tanigawa, *J. of Nuclear Material*, **85 & 86**, 781 (1979)

[1] M.Fleishmenn and S.Pons. *J.Electroanal.*