PRODUCING A RADIOACTIVE SOURCE IN A DEUTERATED PALLADIUM ELECTRODE UNDER DIRECT-CURRENT GLOW DISCHARGE

NUCLEAR REACTIONS IN SOLIDS

KEYWORDS: *autoradiography, nuclear reactions in solids, glow discharge*

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Anomalous gamma emission was rarely observed during direct-current glow discharge in ~3 Torrs of deuterium gas using a deuterated palladium foil cathode. Autoradiography after the discharge experiment showed that isotopes with low- and high-energy radiation components were produced before or during the discharge. The palladium foil after the anomalous gamma-ray emission was analyzed by secondary ion mass spectroscopy, which revealed a considerable increase in the content of iron and copper on the surface.

I. INTRODUCTION

Among several experimental methods for nuclear reactions in solids, gas glow discharge has the advantage of involving less contamination in the reaction vessel in contrast to other methods. The method has been expected to yield higher reproducibility in the analysis of the electrode surface, near which is thought to be the center of the reaction. The glow discharge method has revealed production of ^{4}He (Ref. 1), tritium,[2] and many kinds of elements[1,3] in the D-Pd or H-Pd system. Excess energy of ~2 W (Refs. 4 and 5) in the D-Pd or H-Pd system and gamma rays[6] in the D-Pd system have also been observed during discharge. X rays[7] from the Pd deuteride/hydride have been detected after discharge. Furthermore, several kinds of elements[8,9] and ^{4}He (Ref. 9) have been observed in the Pd deuteride/hydride without discharge. Li et al.[10] have identified two kinds of excess heat in a gas-loaded D-Pd system.

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As most of the reaction probe systems include a preamplifier that would be affected by electromagnetic interference, another supporting detection method free from such interference should be employed as well. One available for the supporting methods is autoradiography, which includes use of X-ray film as a photon detection passive device. This method has shown the production of tritium,[1] beta emission[1] from the Pd deuteride after discharge, and beta emission[4] from the Pd deuteride/hydride during discharge. Some anomalous emission from the Pd deuteride/hydride has been detected without discharge by this method.[11] Autoradiography has also been applied to detect radiation from protons impinging on the Pd hydride.[12] In this study, the authors present the result of autoradiography using highly sensitive monochromatic negative film instead of X-ray film.

II. EXPERIMENT

The reaction is carried out in a test cell, presented in Fig. 1. The test cell has a cylindrical shape with a volume capacity of 80 cm^3, which consisted of a side Pyrex cylindrical window and upper and lower brass flanges. A Viton O-ring was used in a properly designed lower brass flange. The cell can be connected through a manifold to a gas cylinder containing deuterium gas, which enables flushing and filling of the reactor cell with ~3 Torrs of deuterium gas. Glow discharge takes place between two dissymmetrical electrodes: one 10-mm diam rod made of brass, the end of which is covered with 20-μm-thick Au foil and the other the end of which is covered with a Pd foil. The gap spacing is 15 mm. The construction makes it easy to observe the inside of the cell. The 10-mm-diam, 0.1-mm-thick circular Pd foil cathode (99.99% pure) was prepared using the following procedure. First, the Pd foil was washed with aqua regia for 30 s and was

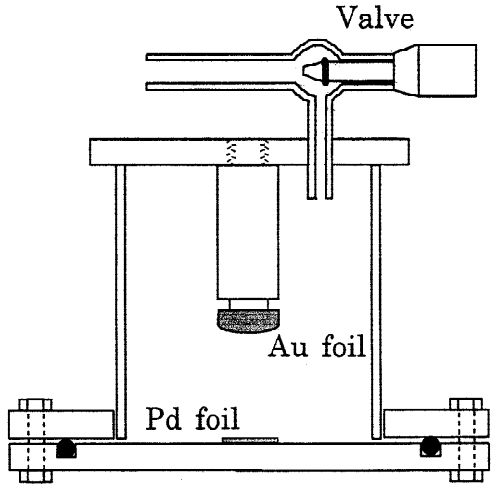

Fig. 1. Test cell.

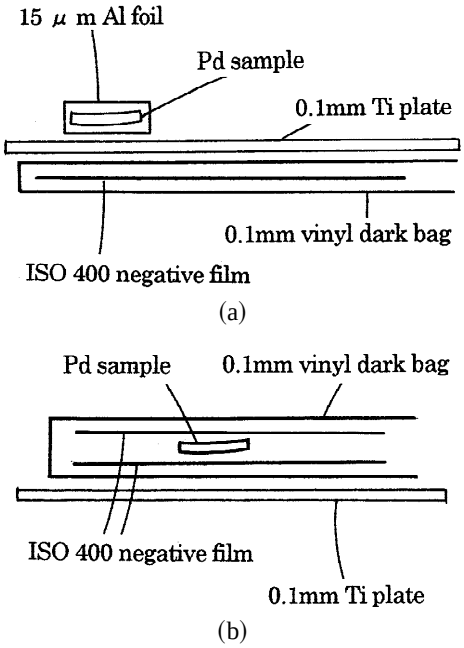

Fig. 2. Autoradiography of (a) one cross section of film arrangement and (b) another cross section of film arrangement.

vacuum annealed at 800°C for 3 h under $\sim 10^{-3}$ Torrs and then was cooled for 8 to 10 h to room temperature, followed by loading of D_2 gas (99.6% pure) under 6 atm of pressure for ~24 h. Next, the Pd foil cathode was set on the bottom of the cell, followed by filling the cell with ~3 Torrs D_2 gas. The deuteron-to-Pd loading ratio was determined from the change in weight to be ~0.6. The X-ray diffraction method showed the Pd lattice after the loading of a mixture of alpha and beta phases. The impurities in the Pd were typically Pt (0.1 ppm), Rh (1.8 ppm), Ag (1.5 ppm), Si (2.1 ppm), Mg (1.1 ppm), and numerous other metals with lesser concentrations. The tritium concentration in the D_2 gas was <0.25 nCi/cm^3.

The Pd foil cathode was grounded, and the rod anode was connected to the positive terminal through a 238-kΩ current-limiting resistor. External metering was provided for glow discharge current and voltage. A positive direct-current (dc) of 500 to 1600 V was applied to the rod electrode to start dc glow discharge between the top of rod and the Pd foil. The discharge lasted for 1 h. The discharge condition accompanying the dc current of some milliamperes was kept for the period. A total of 105 discharge experiments was performed.

A gamma-ray measurement system was used to detect the excess high-energy photons from the nuclear reaction in the Pd foil electrodes. The system consisted of a Na-I scintillation counter, an amplifier, a multichannel analyzer (MCA), and a personal computer (PC). A signal from the counter was fed to the MCA through the preamplifier and the amplifier. The counts were stored on a floppy disk using a PC. The counter head was set perpendicular to and 10 mm away from the side of the test cell. The gamma-ray measurement continued during the dc voltage application period of 1 h.

After the measurement, the Pd foil was also autoradiographed to detect gamma- and X-ray photons and charged particles using monochromatic negative film as a passive detection device. One of the film arrangements for the autoradiography is shown in Fig. 2a, where the Pd foil was set on 100-μm-thick titanium foil. A sheet of black-and-white negative film[a] was set on the other side of the titanium foil to detect photons originating from a radioactive source produced in the Pd foil during the dc glow discharge period. The Pd was occasionally set near the rim of the film to see far into the blackening area within the film size. The Pd foil was lapped in a 15-μm-thick Al foil to prevent its surface from contamination. The film was enveloped with a small 100-μm-thick polymer (vinyl) dark bag. The whole arrangement shown in Fig. 2a was kept in a dark box to avoid unexpected photons from the outside during exposure time at room temperature. The film exposure time was 3 to 8 days. The film developing was enhanced ~8 times greater than usual by increasing the developing time to 8 min and the developing temperature to 27°C.[b] In another case of autoradiography, the Pd foil was directly sandwiched by two sheets of the negative film without the Al foil, as shown in Fig. 2b. In other words, this arrangement gives the contact image of a 0.1-mm-thick, 10-mm-diam deuterated Pd foil. Autoradiography for several Pd hydrides without the discharge experiment was also performed.

[a] The film was ISO 400, Fuji Photofilm Company, Neopan 400 Presto.

[b] Fuji Photofilm Company, Super Prodol was used.

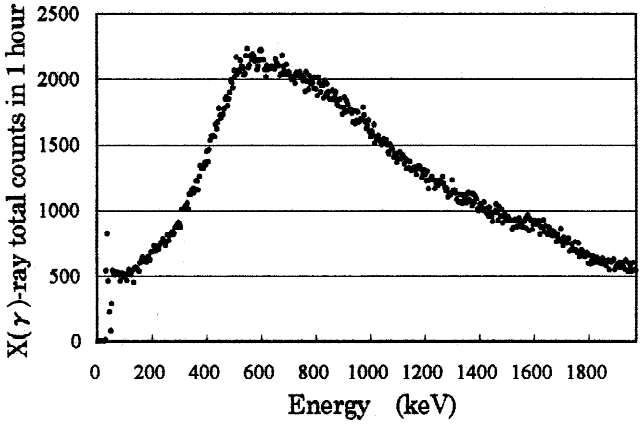

Fig. 3. Gamma-ray spectrum under a nondischarge condition.

Secondary ion mass spectroscopy (SIMS) and electron probe microanalysis (EPMA) for randomly selected areas of particular interest for Pd foil was made after the experiments.

III. RESULT AND DISCUSSION

III.A. Gamma-Ray Spectroscopy

The gamma-ray spectrum under a nondischarge condition is shown in Fig. 3 as the background spectrum. A similar spectrum was observed for most of the runs under glow discharge conditions with the D-Pd system, which indicates that only the background was observed and no gamma-ray emission was detected during the 1-h discharge period. However, anomalous peaks in the spectrum were observed in 4 runs out of a total of 105 runs. A typical spectrum with the anomalous emission peak is shown in Fig. 4, where the peak appears at 106 keV under dc 660-V application using a Pd foil with a loading ratio of 0.69. A small peak at ~70 keV was observed in 2 runs with loading ratios of 0.63 and 0.69 under 1600- and 1400-V application, respectively. Two peaks at ~70 and 100 keV were observed in a run with a loading ratio of 0.71 under 760-V application. It seems that the emission spectra are not caused by the electromagnetic interference and that a higher loading ratio seems to be advantageous for the reaction but higher voltage is not, even though the number of positive runs is low. Miles and Bush[13] have also observed anomalously high radiation counts using Geiger-Mueller detectors as well as sodium iodide detectors during electrolysis experiments with Pd cathodes in heavy water. Here, the Pd foil that gave the emission peak at 106 keV in the gamma-ray spectrum is designated "Pd-106-keV." Neutron detection using the ^{3}He thermal neutron detector did not yield any positive results for the total of 105 runs.

III.B. Autoradiography

All the Pd samples after glow discharge were also autoradiographed using monochromatic negative films. The autoradiograph obtained by Pd-106-keV is shown in Fig. 5, where the film arrangement used is that shown in Fig. 2a. The strong blackened part in the film with the white part shown in the left side on Fig. 5 corresponds to the edge of the Pd foil. The radiation was strong enough to penetrate three piled-up films: one 15-μm aluminum foil, one 100-μm titanium foil and one 100-μm polymer (vinyl) film. It is not likely that alpha or beta particles penetrated the entire 215-μm-thick solid, except with extraordinarily high energy. Thus, the exposure was due to gamma- or X-ray emission from the Pd foil. Another broad exposure area is seen in the right side of Fig. 5, where two circular interference patterns are observed. (In addition, there are several lines locally

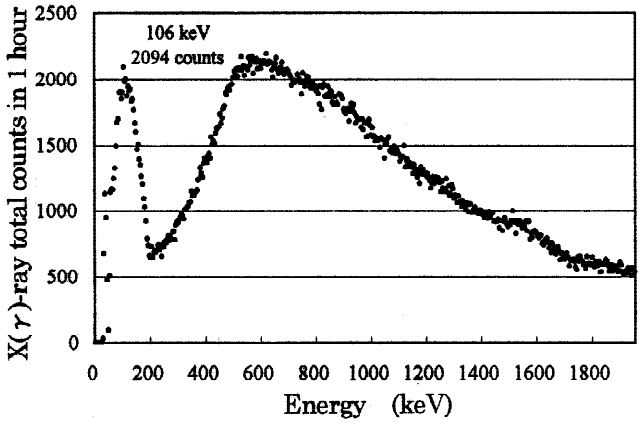

Fig. 4. Gamma-ray spectrum with an anomalous emission peak under a dc glow discharge condition.

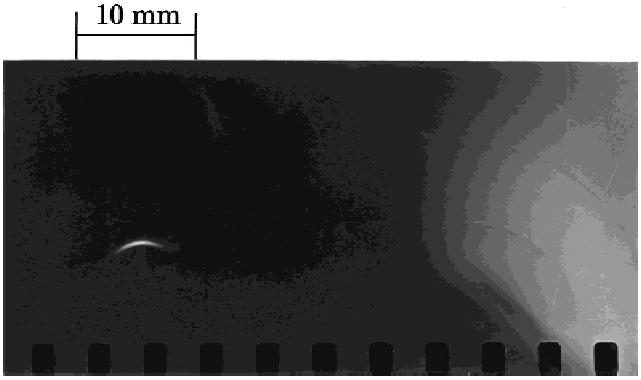

Fig. 5. The autoradiograph of the Pd-106-keV sample by the first film arrangement (Fig. 2a) detecting strong radiation.

generated by scratching.) The mechanism responsible for this broad exposure area is not understood at present. Such strong radiation was obtained only by this single Pd foil of Pd-106-keV. The other three Pd samples, which presented small emission peaks in the gamma-ray spectrum, produced no film blackening for the series of film arrangements shown in Figs. 2a and 2b. Even though no emission peak in the gamma-ray spectrum was observed during glow discharge, some of the Pd foils after the discharge produced weak film blackening using the Fig. 2b film arrangement.

A typical autoradiograph of weak radiation detection is shown in Fig. 6, where film-blackening parts seen on both films correspond to the edge of the Pd foil. In addition, several more weak blackening parts in the shape of an arc are seen on both the films. No clamp was used to fix the position of the Pd. It was ensured that the external pressure of several kilograms did not produce any film blackening. Thus, the blackening might be explained by the action of ionizing radiation, which can be alpha particles, beta rays, or low-energy X rays. However, most Pd foil produced no film blackening, which means the radioactive isotopes with low-radiation energy are a volatile substance, probably tritium. Szpak et al.[14] have precisely investigated tritium production in a D-Pd system for an electrolysis experiment. Thus, the blackening of the film by the low-radiation energy would be due to bremsstrahlung caused by the deceleration of electrons in the Pd foil near its surface, generating photons of energy limited to ~10 keV. The arc shape shown in Fig. 6 is supposed to be produced by interference of the X rays. The two autoradiographs indicate that isotopes with high- and low-radiation energies are considered to be produced before or during glow discharge.

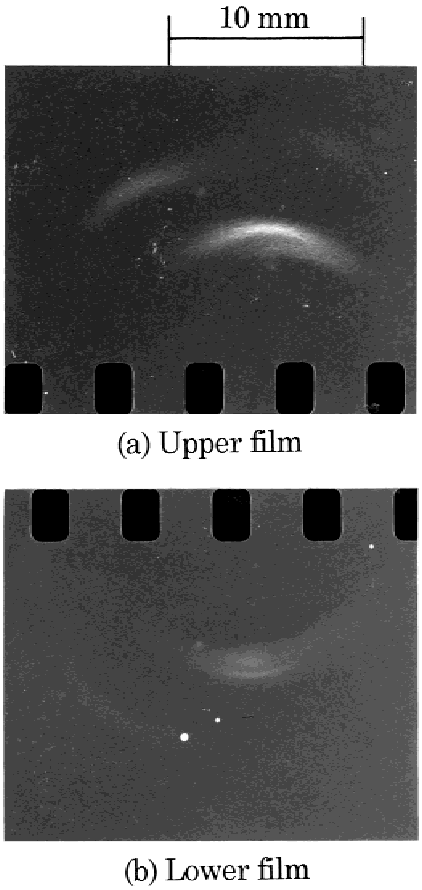

Fig. 6. An autoradiograph by the second film arrangement (Fig. 2b) detecting weak radiation.

Savvatimova et al.[1] also have observed soft and hard components of radiation after a deuterium glow discharge experiment but reported that the components can be betas from tritium with energies of 20 keV and 0.1 to 0.5 MeV, respectively.

Miley[15] has reported high-energy radiation and lower-energy (~20-keV) X-ray and/or beta emission in an electrolytic cell experiment using cathodes coated with thin metallic films. Dufour et al.[4] also reported electron emission with 50-keV energy during arc discharge in deuterium gas and stronger blackening in deuterium gas than in hydrogen gas.

In the present experiment, weak film blackening was also observed for deuterated Pd foil without discharge. The film shows weak but uniform exposure over the entire sample on either side. Such autoradiographs were first observed by Rout et al.[11,16,17] This indicates that loading of D_2 itself would introduce formation of a small amount of tritium. Similar blackening of film was observed using hydride Pd foil without discharge. However, no difference in blackening could be observed between hydrogen and deuterium loading as reported by Rout et al.[11] The film was kept in the atmosphere of deuterium gas for 10 days, and no blackening was observed, which indicates that the film used in the present study was not sensitive to the D_2 gas.

III.C. Secondary Ion Mass Spectroscopy

The primary ion in SIMS was ^{69}Ga, the counting time was 5 min, and the measured area was 80×80 μm for the entire spectroscopy. It was difficult to recognize any increase in counts of any element, except those of mass 27, by SIMS after most discharge experiments. Considerably high counts of mass 27, probably corresponding to Al, was sometimes observed; the Al might be a production element. Further, a marked increase in the counts of ^{56}Fe and ^{63}Cu was observed for Pd-106-keV.

Table I shows counts of ^{56}Fe, ^{63}Cu, and ^{69}Ga atoms by SIMS for eight Pd blank samples as background. These Pd samples were prepared by the same procedure as that of the foreground Pd foils but without D_2 loading and the discharge. A discharge test using a similar Pd foil was also performed without D_2 loading, which showed results similar to SIMS (see Table I). Contamination due to atmospheric exposure seems to be low.

TABLE I

Counts of ^{56}Fe, ^{63}Cu, and ^{69}Ga by SIMS for Eight Pd Blank Samples

Sample Number	^{56}Fe	^{63}Cu	^{69}Ga
B1	1604	833	53 214
B2	2386	1068	53 812
B3	499	582	119 093
B4	3185	1097	118 239
B5	460	546	103 738
B6	<2530	631	96 408
B7	<674	452	63 644
B8	<914	486	71 971

Table II presents the SIMS counts of the three elements for five randomly selected areas on Pd-106-keV. It is difficult to recognize the exact increase in the counts of ^{56}Fe and ^{63}Cu for Pd-106-keV by comparing Tables I and II because of the fluctuation of the counts of ^{69}Ga. The fluctuation is caused by a change in the fine features of the measured area of the Pd surface from place to place and also by an amplitude change in the primary ^{69}Ga ion current of SIMS. Therefore, the ratio of counts of an element to those of ^{69}Ga would fairly indicate the change in counts of the element. The counts of ^{56}Fe and ^{63}Cu, shown in Tables I and II, divided by those corresponding to ^{69}Ga times 1000 are presented in Tables III and IV, respectively. One can see big differences between the numerical values in Tables III and IV; Pd-106-keV shows an increase in the ^{56}Fe content several tens of times. A considerable increase in the content of ^{63}Cu is also seen. Also, Table III shows less contamination with Fe and Cu from the test vessel which consisted of brass flanges.

EPMA for Pd-106-keV also shows the uniform existence of ^{56}Fe and ^{63}Cu over the front portion exposed to discharging. The natural isotope ratios of ^{65}Cu to ^{63}Cu and ^{57}Fe to ^{56}Fe are 0.446 and 0.02, respectively. However, the obtained ratio of ^{57}Fe to ^{56}Fe for Pd-106-keV was in the 0.309 to 0.370 range and its average was 0.340. To the contrary, the obtained ratio of ^{65}Cu to ^{63}Cu agrees with the natural isotope ratio. The anomalous increase in the content of Fe and Cu is consistent with the research of Miley,[15] Mizuno et al.,[18] and Ohmori et al.[19] Mizuno et al.[18] investigated the reaction products with mass numbers from 1 to 208, including Fe and Cu, on Pd cathodes after heavy water electrolysis for 1 month. Ohmori et al.[19] reported the Fe production during light water electrolysis using gold cathodes. Miley[15] has shown that the highest yield elements typically fall into mass bands lying at $A \sim 22$ to 23, 50 to 80,103 to 120, and 200 to 210.

All the results suggest that nuclear reactions possibly occurred in the narrow near-surface layer, occasionally producing new impurity elements of ^{56}Fe and ^{63}Cu. Miley,[15] in particular, studied thin metallic films and the reaction at the cathode surfaces and interfaces. The radioactivity of the sample and the large impurity concentration observed in this study may be a result of a nuclear reaction different from those that occurred in plasma in a high-energy region. From the point of view that the Pd hydride also yields film blackening, protons and deuterons should play a similar role in the reaction.

TABLE II

Counts of ^{56}Fe, ^{63}Cu, and ^{69}Ga by SIMS for Five Selected Areas on the Pd-106-keV Sample

Area Number	^{56}Fe	^{63}Cu	^{69}Ga
A1	108 785	533	57 140
A2	104 688	13 088	153 940
A3	888	11 089	5 225
A4	243 382	705	100 307
A5	48 329	1 759	25 904

TABLE III

The Counts of ^{56}Fe and ^{63}Cu Each Divided by That of ^{69}Ga Times 1000 for Eight Pd Blank Samples

Sample Number	$(Fe/Ga) \times 1000$	$(Cu/Ga) \times 1000$
B1	30	16
B2	44	20
B3	4	5
B4	27	9
B5	4	5
B6	<26	7
B7	<11	7
B8	<13	7

TABLE IV

The Counts of ^{56}Fe and ^{63}Cu Each Divided by That of ^{69}Ga Times 1000 for Five Selected Areas on the Pd-106-keV Sample

Area Number	$(Fe/Ga) \times 1000$	$(Cu/Ga) \times 1000$
A1	1904	9
A2	680	85
A3	170	2122
A4	2426	7
A5	1866	72

IV. CONCLUSIONS

The nuclear reaction in Pd deuterated cathode foil during dc glow discharge in a 3-Torr deuterium gas atmosphere was investigated. No neutron emission was observed during the discharge. However, emissions of gamma rays with energies of 70 and ~110 keV were observed 4 runs out of a total of 105 runs. The emission with 106-keV peak energy in the gamma spectrum was remarkably pronounced.

The autoradiograph for the Pd foil after discharge sometimes yielded film blackening, which means that radioisotopes were produced before or during the discharge. In particular, the radiation from the Pd-106-keV was strong enough to penetrate an entire 215-μm-thick solid. This radiation is considered to consist of X rays or gamma rays. Even though no gamma-ray emission was observed during the discharge, some Pd foils gave weak film blackening when the films were placed directly on either side of the Pd foil. This indicates that most of the radiation from the Pd foil after discharge was weak, so that it was impossible to penetrate a 15-μm Al foil. The weak film blackening could be explained by the action of ionizing radiation, which can be alpha particles, beta rays, or low-energy X rays. X rays due to bremsstrahlung seem to be most plausible. Thus, the result from the autoradiography likely shows production of isotopes with two components of radiation. The weak film blackening was always observed for the deuterated Pd foil without the discharge. Similar blackening was also observed using the Pd hydride. From these results, protons and deuterons would play similar roles in the reaction.

The Pd-106-keV sample was analyzed by SIMS, and the result was compared with those of blank samples. The Pd shows a considerable increase in the counts of ^{56}Fe and ^{63}Cu. All the results give credence to the suggestion that nuclear reactions possibly occur in the narrow near-surface layer, occasionally producing impurity elements of ^{56}Fe and ^{63}Cu.

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