MATERIAL BEHAVIOUR OF HIGHLY DEUTERIUM
LOADED PALLADIUM BY ELECTROLYSIS

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Abstract
Studies on several kinds of palladium cathodes have been conducted using electrochemical cells using LiOD/D2O electrolyte to necessary and sufficient conditions for attaining high deuterium loading. Comparative observations of microstructure and analysis of surface impurities have been carried out on palladium specimens with various pre-electrolysis treatments. Single crystal samples of Pd absorbed deuterium rather slowly, but nevertheless reached comparatively high 0.89 D/Pd loading ratio. Many fine slip band structures were observed on the surface, and several micro-cracks existed in the crystal of post electrolysis specimens. High purity (>99.99%) polycrystalline Pd samples with surface purification treatment such as annealing at 850-1000 C in ultrahigh vacuum, also showed high (0.91 in max.) loading characteristics. Thermal etching effects were observed on the surface of annealed specimens at higher temperatures and high vacuum conditions. Surface micro-cracks along the grain boundaries as well as blistering of the electrode surface were observed in some cases. Surface impurities analysis showed that Li atoms penetrate into the Pd cathode to a depth of several hundred to a thousand Angstroms from the surface. From these observations and analysis of various processed and treated Pd specimens, the material characteristics of Pd cathode achieving high loading ratio are discussed.

1. Introduction
A research and development project, referred to as the “New Hydrogen Energy” project [1], was started in Japan in November 1993, with the main goal of reproducing and verifying the existence of excess heat generation during electrolysis in Pd-LiOD systems.

It has been supposed that the reproducibility of these phenomena is mainly dependent upon achieving control of cathode material properties as well as the electrolysis environment. It has been pointed out by several observers that attaining a deuterium loading ratio (that is, the ratio of deuterium to palladium atoms) greater than 0.85 is a prerequisite for observing excess heat generation phenomena [2][3]. Thus, achieving high reproducibility of anomalous effects depends upon achieving reproducible high deuterium loading ratios.

Material development has proceeded according to this concept. Therefore, material observation and analysis using various techniques has been emphasised in this R&D project.
2. Experimental Procedure
   a. Electrolysis Cell and System. Deuterium loading experiments are carried out to verify the excess heat generation during the electrolysis of heavy water with Pd electrode using fuel cell type electrolysis cells [4]. A schematic diagram of the electrolysis cell is shown in Fig. 1. The inner wall of the cell body containing 1 M LiOD/D2O electrolyte is coated with a Silicon based ceramic film. The Pd cathode, fuel cell anode, reversible hydrogen electrode and thermocouple are fixed in the cell body. Electrolysis is performed with a constant direct current and the current value is changed after equilibrium conditions have been well established for the temperature of electrode, electrolyte and gas phase and deuterium over-voltage at the cathode. The deuterium loading ratio, D/Pd, is determined from the following equation:

\[
\frac{D}{Pd} = -2V \left( \frac{P_o}{T_o} - \frac{P}{T} \right) nR
\]

where \(V\) is the internal gas phase volume of the cell, \(n\) is the total number of mols of metal atoms in the Pd cathode, \(R\) is the universal gas constant, \(P\) is the deuterium gas pressure, \(T\) is the deuterium gas temperature, and \(P_o\) and \(T_o\) refer to the initial values of \(P\) and \(T\) prior to electrolysis.

b. Material Preparation. Various Pd cathode materials are prepared and examined to determine their suitability for achieving high deuterium loading. Pd materials and electrolyte used in the series of experiments are tabulated in Table 1. A commercially available rod (TK-A) is cast in a radio frequency induction-heated furnace in air with an oxidation resistant material. It is then worked by a swaging machine at ambient temperature. Single crystal (TK-AS) was prepared using the floating zone melting method in an argon atmosphere using a TK-A rod as the source material. High purity (>99.995) rods (TK-VA) are cast in vacuum and worked at room temperature. The higher defect density surface zone is removed by machining the outer 200 microns. Other high purity (>99.99) rods (JM-Z) were cast in a hydrogen-nitrogen atmosphere, and worked and annealed before final 20% reduction. After electrodes are machined to final dimensions (4.0 mm x 20 mm length), the surface is polished using diamond paste or diamond spray, and the surface is cleaned with acetone, ethanol, and purified water in an ultra-sonic cleaner. Several finish treatments are examined to remove surface impurities and to make a clean activated surface. Both acid etching for ten minutes in concentrated aqua regia and high temperature vacuum annealing (~850-1000 C for 10 h in a <5 x 10^6 vacuum) have been used. Heat treatment under high vacuum and high temperature have both effects of recrystallisation and surface cleaning by thermal etching.

For cold-worked specimens, a 200 C vacuum process is used to remove hydrogen from the Pd cathode.

c. Observation methods and impurity analysis. Pre-electrolysis and post-electrolysis observations of the microstructure of the specimens are performed using OM, SEM, and FE-SEM, and the impurity analysis are carried out with AES, SIMS and EPMA. The measurement of lattice parameter and phase change are observed by X-ray diffraction. An in situ video observation method of surface microstructure has been developed to investigate microstructural change during electrolysis process and to observe deuterium bubble formation and release process.

3. Results of the deuterium loading
   A typical history of current density, D/Pd ratio, input power and excess heat are shown in Fig. 2 for the case of TK-VA-3. At the beginning of electrolysis the current density was set at 50 mA/cm^2 for 6 days, and then the current density was changed step by step to 100, 200, 400, and 600 mA/cm^2 for two days at each level. After this current cycle, the current density was decreased abruptly to 200 mA/cm^2 and again stepped up to 800 mA/cm^2, and followed by additional high current pulse or
ramps. These changes of electrolysis condition were performed to investigate the dependence of D/Pd ratio and excess heat generation upon current density. In this case, the maximum D/Pd reached 0.91 at 200 mA/cm² and 0.89 at 800 mA/cm², 28 and 24 days after the start of electrolysis respectively. Excess heat generation phenomena has been reproducibly observed with suitable material preparation and treatment in the fuel cell type electrolysis cells.\[3\]

Loading ratios attained by similar electrolysis condition described as above, are tabulated also in Table 1 for several Pd materials.

4. Results of material observations and analysis.
   a. Microstructural change during loading and deloading. Single crystal Pd samples (TK-AS) absorbed deuterium slowly. However the maximum loading ratio reached the rather high value of 0.89. Many regular slip band bands about 2 μ in breadth, along the (111) plane were observed on the surface as shown in Fig. 3. The x-ray diffraction pattern of the post electrolysis specimen shows the sample no longer has a purely single crystal structure. Several internal crack like defects are observed in the post electrolysis single crystal specimen as shown in Fig. 4. These might be caused by the deformation of the crystal due to deuterium absorption and transitions between the \( \alpha \) and \( \beta \) phases.

   The surface structure of high purity polycrystalline Pd (TK-VA) after high temperature vacuum annealing is shown in Fig. 5a. Grain boundaries and fine surface structures are observed in the grains as shown in Fig. 5b, which were probably formed by thermal etching in high vacuum. Fig. 5c shows the surface structure of TK-VA-2 after electrolysis. Several cracks along the grain boundary are observed and fine slip band bands are also observed in the crystal grains. The basic mechanism of the formation of slip bands is presumed to be the same as for the case of single crystal samples.

   The microstructure of EH-L1 specimens before electrolysis and after are shown in Fig. 6a-c. The average grain size is about 200 μ. Sub-grain-like fine structures are observed at the inside of initial grains on the etched surface. Fine granulation seems to be proceeded by the transition between \( \alpha \) and \( \beta \) phases.

   Figs. 7a-b show the cross sectional views of a relatively low loading state (D/Pd=0.20). The \( \alpha + \beta \) phase region progresses radially toward the centre and fine granulation is also observed in the initial grains. Diffusion enhancement at grain boundaries, which is normally expected, seems to have less effect in this system.

   Fig. 8a-b show that blistering due to deuterium gas occurred on the surface of electrode during electrolysis in some annealed specimens. Clear cracks along the grain boundaries were formed on the top of the blistering. This phenomena may be explained by assuming existence of some kind of defect such as closed pore, inclusion, or plane shape defects near the surface before electrolysis. Deuterium gas may accumulate in the defect, and as a result the gas pressure increases several hundredfold. The annealed surface is then deformed by blistering.

   b. Surface impurity analysis. Fig. 9a shows the AES surface impurity analysis after electrolysis. Impurities such as S, Cl, C, and O are detected in most post electrolysis specimens. However it is confirmed by an ion-sputtering method that the impurity layer is less than 20 Angstroms thick. The existence of C and O are confirmed by EPMA analysis. Fig. 9b shows the depth profile of the near surface region of the palladium cathode by AES. The penetration of Li atoms from LiOD into the Pd cathode is confirmed by SIMS. The penetration depth ranges from several hundred to a thousand Angstroms, according to the depth profile analysis.

5. Discussion

Absorbed deuterium into the Pd crystal will be expected to occupy the octahedral sites of fcc Pd lattice for D/Pd ratios up to unity, and tetrahedral sites for over unity. It is believed that the
tetrahedral site of Pd acts as a transient site for the diffusion process. As an analogical model of deuterium loading, it could be considered that the Pd lattice forms a volume for the deuterium atoms (ions). The D/Pd ratio can be calculated as the integral difference of inlet flow and outlet flow of deuterium atoms in this specific volume element. To first order, during steady-state electrolysis, inlet flow and outlet flow will be mainly dependent on the surface conditions, the concentration of deuterium atom density and the electronic potential field on the Pd electrode surface, and surface microscopic and macroscopic structures. The inlet flow and outlet flow are considered to be controlled by absorption, desorption and diffusion through several kinds of paths in the Pd material. The effect of the value of the diffusion rate on the maximum loading ratio would be somewhat complicated; however the diffusion rate is generally small. Diffusion is enhanced by introducing lattice defects such as point defect, dislocation and grain boundary defects. The migration rate of deuterons is increased and saturation of loading ratio is prompted by the introduction of lattice defects. However, the final saturation value of loading ratio will be decreased because the outlet flow responds more sensitively to the state change of flow channels on the surface especially at high loading ratios (D/Pd > 0.8).

From these simplified considerations, the basic requirements for Pd material capable of achieving a high loading ratio are as follows:
1) to have large numbers of vacant absorption sites (O-sites).
2) to have a large absorption area during electrolysis;
3) to minimise dissociation area and prevent the incremental loss of deuterium;
4) to minimise the quantity of dissociated deuterium during the electrolysis process.

Table 2 shows the favourable state mentioned above and the corresponding material treatments. From these considerations, the specification of Pd material and the treatment having high loading ratio have been selected as follows:
A) Specification: (1) Initial purity > 99.99%, (2) vacuum melt, (3) forging and annealing to homogenise, (4) machining the outer 0.2 mm to remove surface defects.
B) Treatment: (1) Surface cleaning and etching by aqua-regia to remove surface impurities,
(2) Ultrahigh vacuum (oil free) high temperature annealing to recrystallise and to form an activated surface.

The TK-VA material series of Table 1 is made on this concept, and achieved the highest loading ratio of 0.91. Further modifications are necessary to prevent blistering, crack formation at grain boundaries, and loading reduction at higher current density. The material must maintain good ductility and resistance against the deformation due to the stress release which accompanies deuterium loading and transformation. The effects of deposition of surface impurity and Li penetration have to be clarified.

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NHE Session

Reference


Table 1 Material list of Pd samples used in experimental series.

<table>
<thead>
<tr>
<th>lot No</th>
<th>purity (major impurities)</th>
<th>cast</th>
<th>working</th>
<th>grinding</th>
<th>polishing</th>
<th>spec. processing</th>
<th>etching</th>
<th>heat treatment</th>
<th>Hv hard.</th>
<th>loading ratio max. B(Pd)(Pd)</th>
<th>D(Pd) range</th>
</tr>
</thead>
<tbody>
<tr>
<td>TK-4</td>
<td>&gt;99.55</td>
<td>RF in air, RT swaging</td>
<td>none</td>
<td>All</td>
<td>O, I</td>
<td>-</td>
<td>as cold worked</td>
<td>100°C evacuated</td>
<td>-</td>
<td>0.95</td>
<td>4.47</td>
</tr>
<tr>
<td>TK-5</td>
<td>&gt;99.9</td>
<td>RF in air, RT swaging</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>single crystal by floating zone</td>
<td>-</td>
<td>-</td>
<td>0.99</td>
<td>0.41</td>
<td>0.45</td>
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<tr>
<td>TK-VA-1</td>
<td>&gt;99.9</td>
<td>RF in vac, RT swaging</td>
<td>5mm dia spray</td>
<td>-</td>
<td>-</td>
<td>as cold worked</td>
<td>100°C evacuated</td>
<td>-</td>
<td>0.95</td>
<td>0.30</td>
<td>0.36</td>
</tr>
<tr>
<td>TK-VA-2</td>
<td>&gt;99.9</td>
<td>RF in vac, RT swaging</td>
<td>5mm dia spray</td>
<td>-</td>
<td>-</td>
<td>as cold worked</td>
<td>100°C evacuated</td>
<td>-</td>
<td>0.95</td>
<td>0.30</td>
<td>0.36</td>
</tr>
<tr>
<td>TK-VA-3</td>
<td>&gt;99.9</td>
<td>RF in vac, RT swaging</td>
<td>5mm dia spray</td>
<td>-</td>
<td>-</td>
<td>as cold worked</td>
<td>100°C evacuated</td>
<td>-</td>
<td>0.95</td>
<td>0.30</td>
<td>0.36</td>
</tr>
<tr>
<td>TK-VA-4</td>
<td>&gt;99.9</td>
<td>RF in vac, RT swaging</td>
<td>5mm dia spray</td>
<td>-</td>
<td>-</td>
<td>as cold worked</td>
<td>100°C evacuated</td>
<td>-</td>
<td>0.95</td>
<td>0.30</td>
<td>0.36</td>
</tr>
<tr>
<td>JN-2</td>
<td>&gt;99.5</td>
<td>RF in vac, RT swaging</td>
<td>none</td>
<td>-</td>
<td>-</td>
<td>as cold worked</td>
<td>100°C evacuated</td>
<td>-</td>
<td>0.95</td>
<td>0.30</td>
<td>0.36</td>
</tr>
<tr>
<td>ELI-1</td>
<td>&gt;99.5</td>
<td>RF in vac, RT swaging</td>
<td>none</td>
<td>-</td>
<td>-</td>
<td>as cold worked</td>
<td>100°C evacuated</td>
<td>-</td>
<td>0.95</td>
<td>0.30</td>
<td>0.36</td>
</tr>
<tr>
<td>HV-1</td>
<td>&gt;99.5</td>
<td>RF in vac, RT swaging</td>
<td>none</td>
<td>-</td>
<td>-</td>
<td>as cold worked</td>
<td>100°C evacuated</td>
<td>-</td>
<td>0.95</td>
<td>0.30</td>
<td>0.36</td>
</tr>
</tbody>
</table>


Fig. 1 Schematic diagram of the electrolysis cell

Fig. 2 Typical history of loading ratio D/Pd, input current, input power, and temperature of Pd cathode (TK-VA-3)
Fig. 3 Many regular slip bands were observed (by FE-SEM) on the surface of post electrolysis single crystal (TK-AS).

Fig. 4 Internal crack-like defect in the post electrolysis single crystal (TK-AS) observed by SEM.

Fig. 5a-c Surface structure of TK-VA annealed at 1000°C x 10 hr in high vacuum (<5 x 10^-6 torr). Grain boundary and fine surface structures are observed in the grain, probably formed by thermal etching in high vacuum (Fig. 5b). Several cracks along the grain boundary and fine slip bands are observed in the crystal grains of the sample after electrolysis (Fig. 5c).
Fig. 6a-c Polished and etched surface structure of cross section of EH-L1 before (6a), and after (6b and 6c) electrolysis. Sub-grain-like fine structures are observed at the inside of initial grains as shown in Fig. 6c.

Fig. 7a-b Cross sectional view of relatively low loading state of TK-VA. The α + β region progresses radially toward centre and fine granulation is advanced.

Fig. 8a-b Blistering due to deuterium gas occurred on the surface of electrode during electrolysis in some annealed specimens (TK-VA). Fig. 8b shows the top structure of blistering and several cracks are formed along to the grain boundary.
Fig. 9a-b AES surface impurity analysis after electrolysis (TK-A). Impurities of S, Cl, C, and O are detected in most post electrolysis specimens (Fig. 9a). Depth profile of palladium atoms on the near surface region after electrolysis is shown in Fig. 9b. The penetration of Li atoms from LiOD into the Pd cathode is confirmed by SIMS analysis.

Table 2 Basic characteristics of high loading material and corresponding treatments.

<table>
<thead>
<tr>
<th>Favorable Material State</th>
<th>Corresponding Treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Make Vacant state of Absorption Site (O-Site)</td>
<td>High purity material. Vacuum melt. and Evacuate at high temp., ultrahigh vacuum</td>
</tr>
<tr>
<td>Remove impurity atoms on O-site</td>
<td>High purity material. Vacuum melt. and Evacuate at high temp., ultrahigh vacuum</td>
</tr>
<tr>
<td>Reduce inclusion / precipitates / closed pore</td>
<td>High purity material. Vacuum melt. and Evacuate at high temp., ultrahigh vacuum</td>
</tr>
<tr>
<td>Remove surface bad impurities</td>
<td>High vacuum &amp; high temp. treatment</td>
</tr>
<tr>
<td>Prevent adsorption of bad impurities</td>
<td>Purification of electrolyte</td>
</tr>
<tr>
<td>(3) Minimize Dissociation Area &amp; Prevent Increment</td>
<td>Surface machining. Annealing stress</td>
</tr>
<tr>
<td>Remove surface macroscopic crack</td>
<td>Vacuum melt. Clean working processing</td>
</tr>
<tr>
<td>Reduce open pore. surface inclusion</td>
<td>Vacuum melt. Homogenized treatment</td>
</tr>
<tr>
<td>Reduce closed pore. defect in near surface</td>
<td>Fine surface polishing</td>
</tr>
<tr>
<td>Reduce surface scratch. roughness</td>
<td>Suitable grain size. Additional cold working</td>
</tr>
<tr>
<td>Minimize Dissociation channel</td>
<td>Homogenization</td>
</tr>
<tr>
<td>(4) Suppress Dissociation Quantity During Electrolysis</td>
<td>Suitable grain size. Additional cold working</td>
</tr>
<tr>
<td>Keep ductility/toughness against deformation</td>
<td>Optimize electrolysis condition.</td>
</tr>
<tr>
<td>Keep high loading ratio at high current density</td>
<td>Optimize electrolysis condition.</td>
</tr>
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