New Internal Friction Peak in Hydrogenated Palladium[†]

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Abstract

Relation between internal friction peak and hydrogen behavior was investigated, as the palladiums containing various aluminum contents were hydrogen-charged at various current densities and then aged at room temperature.

Deformation twins, cracks and the phase transformation from α phase to β phase occurred by hydrogenation, and they depended on the current density and aluminum impurity.

The four internal friction peaks mainly appeared in hydrogenated palladium at 1 Hz. The peak at 80K is related to hydrogen concentration in the α phase or the β phase corresponding Gorsky effect. The peak at 110K is related to cold work peak with hydrogen and dislocation. Another new two peaks were found. The new peaks at 150K and at 170K are considered to be related to the interaction with hydrogen and deformation twin in the α phase and the β phase respectively.

The internal friction peaks were affected by the current density of cathodic charging and aluminum impurity in the palladium. The peak at 80K was predominant for the sample with 0.0283mass% aluminum, the peak at 110K was highest for the sample with 0.01mass% aluminum and the peak at 150K was predominant for the sample with trace aluminum.

The hydrogenation with high current density accelerated the transformation from β phase to α phase during aging at room temperature owing to the high internal stress and dislocation density.

KEY WORDS: (Internal Friction Measurement) (Palladium) (Hydrogenation) (Lattice Parameter) (Deformation Twin) (Aluminum Impurity)

1. Introduction

The palladium-hydrogen phase diagram has been widely studied[1]. Palladium readily absorbs hydrogen forming PdHx, and hydrogen is very mobile within the lattice. Hydrogen atoms produce a distortion of the cubic lattice and plastic deformation in palladium[2,3].

The occlusion and diffusion mechanisms of hydrogen in palladium imply the formation of two phases; α and β phase corresponding to different combinations of hydrogen and palladium atoms.

At room temperature and at concentrations below H/Hd=0.03 the α phase exists only, with a lattice constant of 0.389nm[4]. Above H/Hd=0.6 only the β phase is present with a lattice constant of 0.402nm[4]. At intermediate concentrations the two phase coexist. The phase transformation occurring in this range seems to involve a plastic deformation of the lattice.

In the palladium-hydrogen system, measurements of internal friction have been performed to get information about the diffusion of hydrogen and the interaction of hydrogen with dislocations. The effect of combined action of interstitial and dislocation can give rise in cubic lattices to thermally activated relaxation effects whose characteristics are of great importance to investigate the structural properties.

Recently, Fleischman et.al[5] reported that they observed cold fusion reaction in palladium cylinders electrically charged with deuterium. Jones et al.[6] also observed such reactions in titanium. However the confirmation of these facts has not been done yet.

Hydrogen behavior in palladium has not been clarified yet, because the hydrogen behavior is considered to be affected by the impurities in palladium. For instance impurity such as carbon affects the internal friction peak[7]. In iron the cold work peak of hydrogen with dislocation is also affected by the presence of carbon or nitrogen[8]. In case of titanium, aluminum causes the increase of hydrogen solubility and inhibits the hydride

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precipitation[9]. Palladium is casted in alumina ingot or chromium oxide ingot. Therefore aluminum is contained in the palladium using alumina ingot. However the role of substantial atoms such aluminum to the hydrogen behavior in palladium has not been clarified yet.

The aim of this work is to give some information about hydrogen diffusion and interaction mechanism, measuring the effect of hydrogen impurities upon the internal friction of the specimens submitted to different current densities of cathodic charging and aluminum impurity.

2. Experimental procedure

Three kinds of palladiums containing aluminum were prepared. They were cold-rolled to 0.8mm thick after casting. The Pd-A sample, the Pd-B sample and the Pd-C sample contain 0.0283mass%, 0.01mass% and trace of aluminum respectively. Each palladium is also containing 0.0044mass%Fe, 0.001mass%Au, 0.001 mass% Cu and 0.001mass%Pt. One of Pd-C sample was vacuum-annealed at 673K for 7.2ks in order to decrease dislocation density and hydrogen content in palladium.

The materials were machined into specimens (115mm long, 4mm wide and 0.8mm thick) for X-ray diffraction techniques and internal friction measurement. The specimen surface was finished using acetone after polishing by emery paper of #1500 before the tests.

Hydrogenation to the specimen was carried out using cathodic charging method in a 5% H_2SO_4 aqueous

solution at 800, 2000 and 5000A/m^2 for various times at room temperature below 300K in order to change the surface hydrogen concentration of the specimen. A platinum wire was used as anode..

X-ray line profiles were made by using X-ray diffractometer with copper radiation filtered by nickel. The d spacing and lattice parameter were determined by using the angular position of maximum peak intensity. All the specimens were measured at room temperature below 293K.

The internal friction measurement was performed using an inverted torsion pendulum over a temperature range of 70K to 300K at a frequency of about 1 Hz in the heating rate at 0.02K/s.

The thickness of the specimens before and after hydrogen charging was also measured using micro-meter and the expansion was evaluated by the change in thickness.

3. Results

3.1 Internal friction peak in hydrogenated palladium

Figure 1 indicates the X-ray line profiles as the as-received Pd-A sample was cathodic-charged at 2000 A/m^2. Before charging, the diffraction peaks of α phase only can be observed. As the charging time is 60 sec, both peaks of α phase and β phase are observed. Above the charging time of 10.8ks, the diffraction peaks of β phase only can be observed. Consequently, the hydrogenation to the α palladium causes the phase transformation from α phase to β phase.

Figure 2 shows the relation between the lattice parameter and hydrogen charging time for the Pd-A sample. The lattice parameter of α phase is 0.389nm.
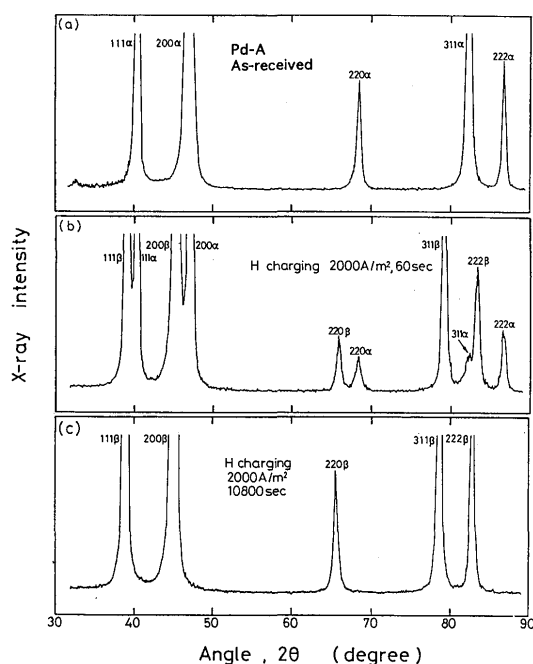

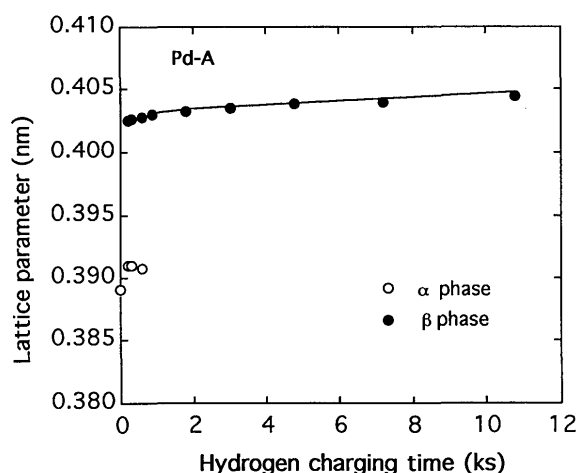Fig. 1 X-ray line profiles as the as-received Pd-A sample was cathodic-charged at 2000 A/m^2.

Fig. 2 Relation between the lattice parameter and hydrogen charging time for the Pd-A sample.
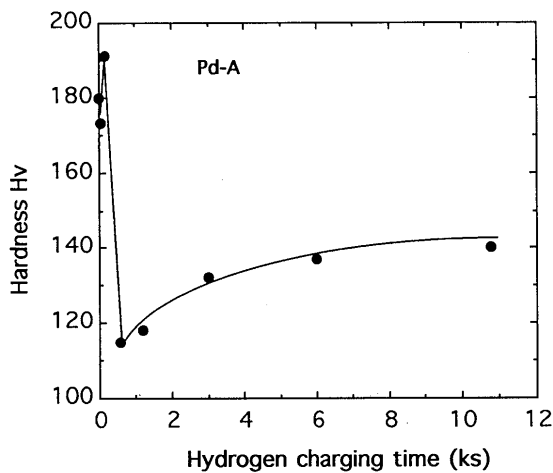
Fig. 3 Relation between the hardness and hydrogen charging time for the Pd-A sample.

The lattice parameter of α phase increases up to 0.391nm and β phase appears at short hydrogen charging time. Above 0.5ks of hydrogen charging time, β phase only is present and the lattice parameter increase from 0.4025nm to 0.4045nm. The volume of α phase is increased 0.5% and that of β phase is increased 0.49% by hydrogenation. The change in volume from α phase to β phase is 3% by hydrogenation.

Figure 3 indicates the relation between the hardness and hydrogen charging time for the Pd-A sample. The hardness of α phase before charging is Hv 180. The hardness of α phase increases a little to Hv 190 at short cathodic charging time, and the transformation from α phase to β phase causes the decrease of hardness. Consequently the hardness of β phase in lean hydrogen concentration is Hv 118. Then the hardness increases with increasing hydrogen charging time and the hardness of the β phase in high hydrogen concentration is Hv 140.

Figure 4 shows microstructures as the as-received Pd-A samples were hydrogen-charged at 2000A/m² for 1.8ks. The three typical microstructures are observed in this sample. Figure 4-(a) shows the microstructure consisting of α phase (white area) and β phase (dark zone). Figure 4-(b) indicates the microstructure showing deformation twin in the α phase and β phase. Figure 4-(c) indicates the microstructure showing cracks in the β phase. Cathodically charged palladium has characterized by the deformation twin and the cracks in the α and β phases.

Figure 5 indicates the change in internal friction peak as the Pd-A sample was hydrogen-charged for various times. Before charging, the internal friction peak can be hardly observed . The three kinds of peaks appear in the temperature range up to 150K such as a peak A, a
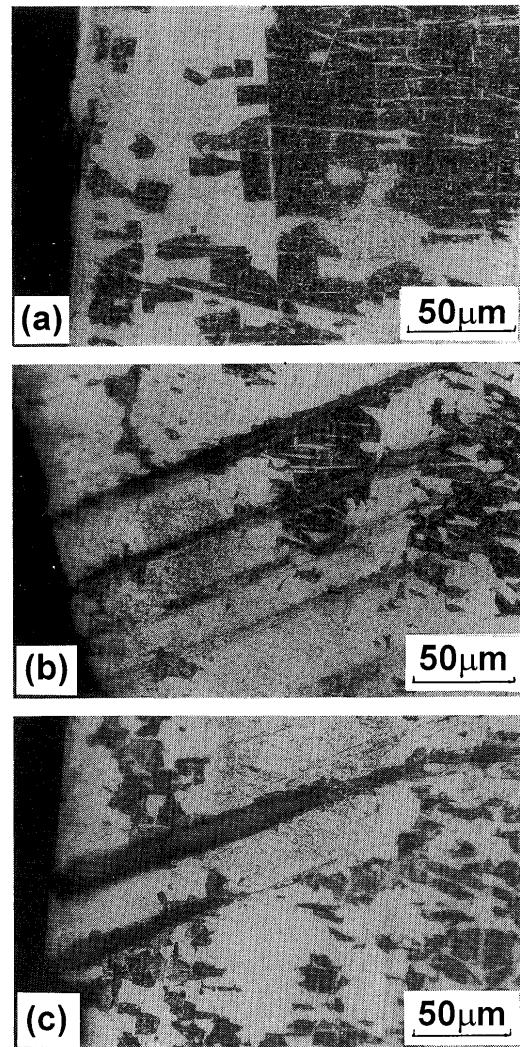

Fig. 4 Microstructures as the as-received Pd-A samples were hydrogen-charged at 2000A/m² for 1.8ks. (a):α+β microstructure, (b):Deformation twin, (c):Cracks within twin

peak B and a peak C by hydrogen charging.

According to Arons et al.[10], the peak A is corresponding to hydrogen concentration and the peak B is the interaction of hydrogen with dislocations. In case of 0.06<H/Pd<0.52, the α phase exists only and the peak A exists at 75K and peak the B exists at 105K (2.7Hz). In case of 0.67<H/Pd<0.68,the β phase exists only and the peak A exists at 80K and the peak B exists at 100K (2.7Hz).

In the β phase the hydrogen atoms occupy randomly the octahedral position in the f.c.c.Pd lattice[8,11]. The peak A is believed to be caused by the stress induced ordering of hydrogen and is Snoek type peak. Snoek peak is generally observed in b.c.c metals. In case of f.c.c. metal, the peak A is considered to be generated by
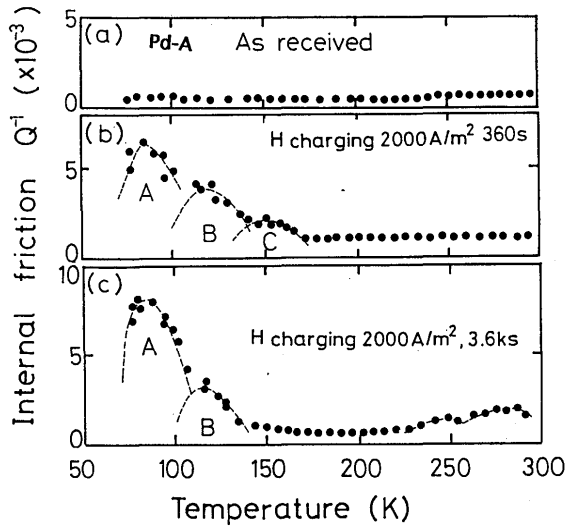
Fig.5 Change in internal friction peak as the Pd-A
       sample was hydrogen-charged for various times.

Fig.6 Relation between change in thickness and
       hydrogen charging time for the Pd-A sample.
       mesurement.

Gorsky effect[12].

After deformation another peak B appeared which was claimed to be the cold work peak (CWP) of hydrogen in palladium[8,11,13]. The height of this peak was strongly reduced by the presence of impurities. In this work, another new peak C and D are considered to be CWP in twined α phase and twined β phase respectively based on the observation in Fig.4-(b).

3.2 Effect of current density and aluminum impurity on internal friction peak

Figure 6 indicates the relation between the change in thickness and hydrogen charging time for the Pd-A sample. As the hydrogen charging time increases, the thickness of the specimen in every current density increases and becomes high up to 10%. The expansion of lattice parameter from α phase to β phase is about 3% as shown in Fig.3.

In case of cathodic charging, hydrogen concentrates toward the thickness direction and considerable plastic deformation and heavy twins are considered to occur in the specimen. This means that inhomogeneous intenal stress and deformation took place in the sample and the degree is considered to be high as the current density increases. The current density affects the hydrogen occlusion rate but the thickness of the specimen is hardly affected by the current density, though the hydrogen concentration near the specimen surface depends on the current density of cathodic charging and the degree of plastic deformation is also considered to be affected by the current density .Consequently, microscopic deformation can be hardly detected by using the thickness.
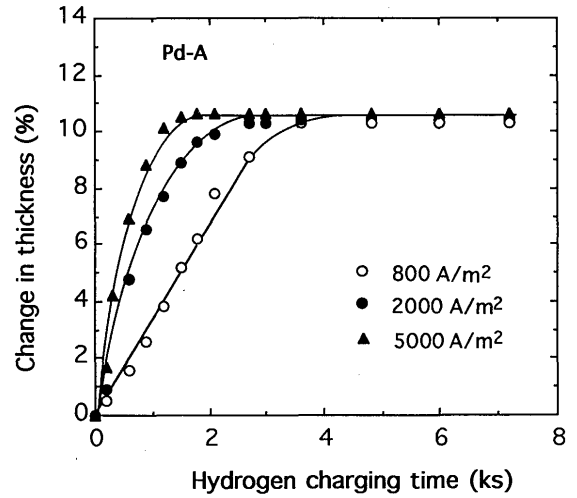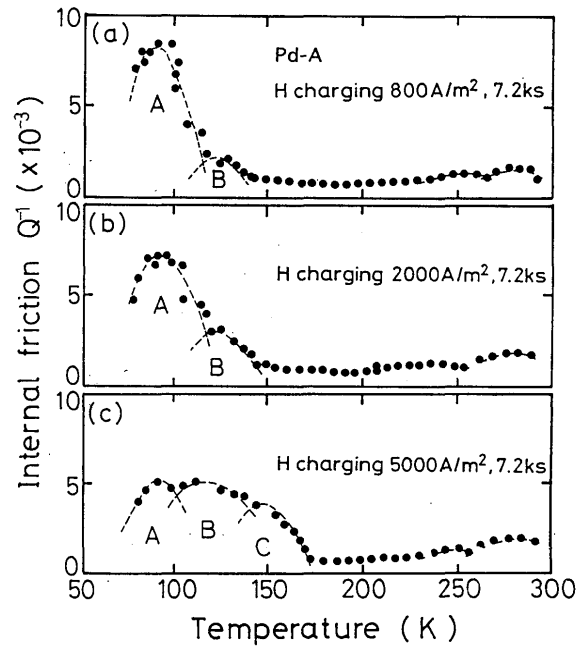

Fig.7 Internal friction versus temperature curves for
       Pd-A sample with 0.0283mass% aluminum.

Figure 7 indicates the internal friction versus temperature curves for the Pd-A sample containing 0.0283mass% aluminum. In case of 800 A/m^2, the peak A is highest and the peak B is also observed. The peak A decrease and the peak B increases with increasing the current density. In case of 5000A/m^2, the peak C corresponding to CWP in twin also appears. Consequently, as the current density is low, the peak A corresponding to hydrogen concentration in the β phase is high. The peak B corresponding to the hydrogen-dislocation interaction is high and furthermore the twin
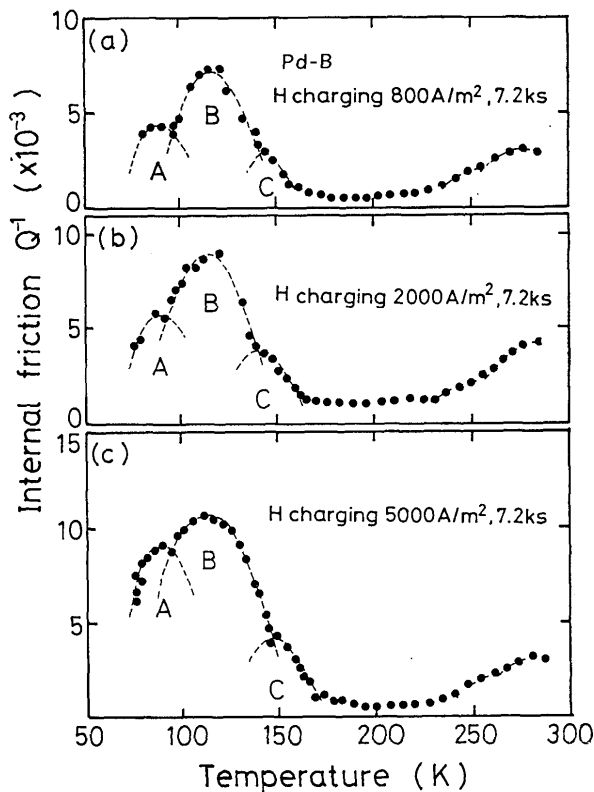
Fig. 8 Internal friction versus temperature curves for Pd-B sample with 0.01mass% aluminum.

Fig. 9 Internal friction versus temperature curves for Pd-C sample with trace aluminum

occurs and the peak C corresponding to the twin and dislocation relationship occurs with increasing the current density.

Figure 8 indicates the internal friction versus temperature curves for the Pd-B sample containing 0.01mass% aluminum. In case of 800 A/m^2, the peaks B is highest and then the peak A and C are present. The height of three peaks increases with increasing the current density.

Figure 9 indicates the internal friction versus temperature curves for the Pd-C sample containing trace aluminum. In case of 800A/m^2, four kinds of peaks are observed. The height of peak C is highest and increases and another B peak decreases with increasing the current density. In this sample, aluminum contains trace and the peak C and D is predominant. Many deformation twin and cracks were obsrved and they increased with decreasing aluminum impurity. Consequently, aluminum strongly affects the internal friction peak and it is concluded that aluminum inhibits the deformation twin in the β phase.

3.3 The internal friction peak in hydrogenated and then aged Palladium
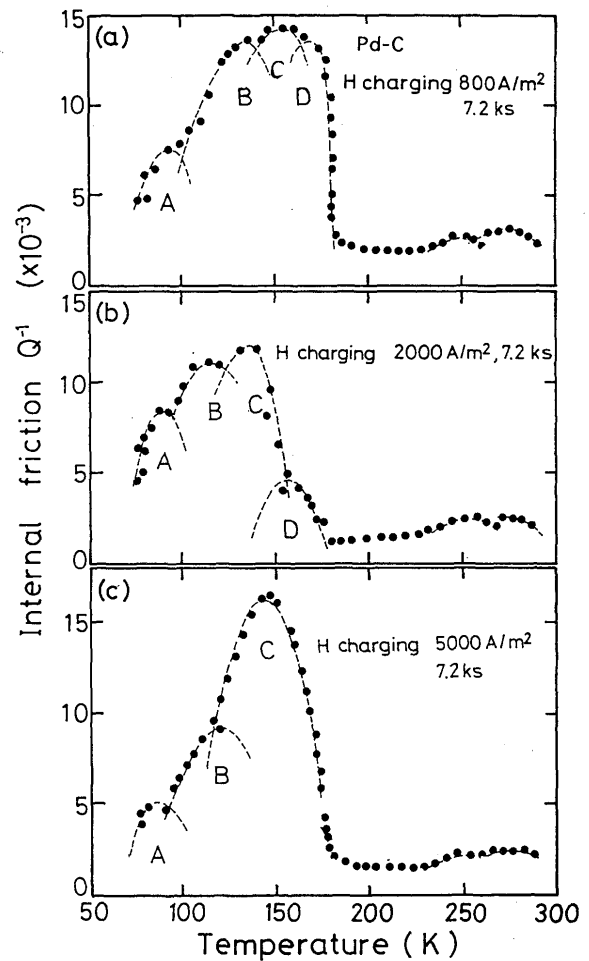
As the hydrogenated β palladium is aged at room

temperature, hydrogen diffusion will occur and escape from the sample surface because of high hydrogen diffusibility,[15]. Then the transformation from the β phase to the α phase is expected to occur.

Figure 10 indicates the relation between the change in thickness and aging time at room temperature for the Pd-B sample. The change in thickness decreases with increasing aging time. This means that the transformation of beta to alpha occurs by aging.

The thickness by cathodic charging was independent of the current density as shown in Fig.6 but the thickness by aging strongly depends on the current density. This means that the internal microstructure, that is, dislocation density and deformation twin increased by cathodic charging and the hydrogen escaping from the sample was accelerated.

Figure 11 indicates the relation between hardness and aging time as the Pd-B sample was hydrogenated at various current densities and aged at room temperature .
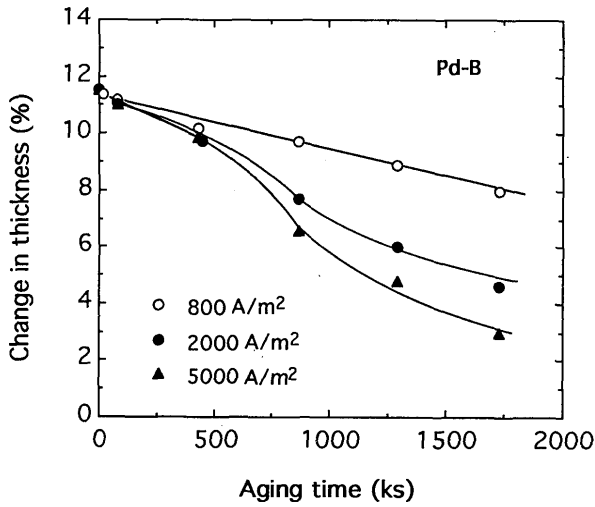
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Fig.10   Relation between change in thickness and aging time, as the Pd-B sample was hydrogenated at various current densities and aged at room temperature.
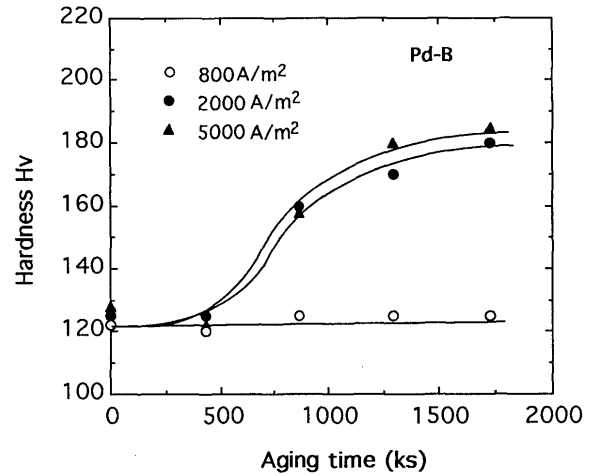

Fig.11   Relation between hardness and aging time as the Pd-B sample was hydrogenated at various current densities and aged at room temperature.

In case of $800A/m^2$, the hardnesses hardly change up to 1700ks of aging. This means that the transformation from the β phase to the α phase hardly occurred. In case of 2000 and $5000A/m^2$, Above 600ks, the hardness increases with increasing aging time, because of the transformation from the β phase to the α phase. It is considered that high current density causes the plastic deformation and twin and then the driving force is high and then the transformation from the β phase to the α phase occurs easily.

Figure 12 indicates the change in the internal friction versus temperature curves as the Pd-B sample was hydrogen-charged and then aged at room temperature. The peaks at 86.4ks aging have not any changed yet as same as Fig.8-(b). In case of 864ks aging, the height of peak B decreases because of low hydrogen concentration and low internal stress. However the height of peak A increases with increasing aging time. This means that the hydrogen evolution occurred from the specimen, the strain decreased, the transformation occurred and the hydrogen concentration in the α phase increased .

Figure 13 indicates the relation between the change in thickness and aging time for the Pd-C sample. In case of the sample annealed at 673K, the change in thickness hardly occurs up to 2300ks. In case of the as-received specimen, the thickness decreases with increasing aging time. The dislocation density is very low for the annealed sample but the density is high for as-received sample that was cold-rolled. The dislocation density is considered to affect the hydrogen evolution behavior.

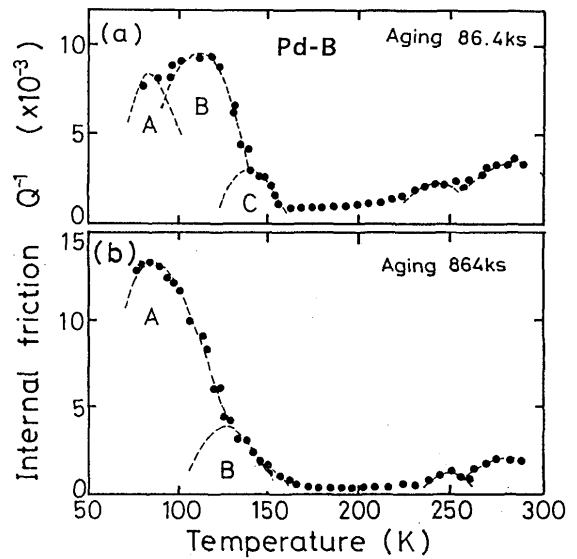Figure 14 indicates the relation between hardness and aging time as the Pd-C sample was hydrogen-charged

Fig.12   Change in internal friction versus temperature curves as the Pd-B sample was hydrogen-charged and then aged at room temperature.

and then aged at room temperature. In case of the sample annealed at 673K, the hardness of hydrogenated sample is lower than that of as-received sample, because the dislocation density is low, and the hardness hardly changes by the aging treatment. However the hardness in the as-received specimen increases with increasing aging time. The increase of hardness means the transformation from the β phase to the α phase.

Figure 15 indicates the X-ray line profiles as the as-received Pd-C sample was charged and aged at room temperature. As the specimen was charged at $2000A/m^2$
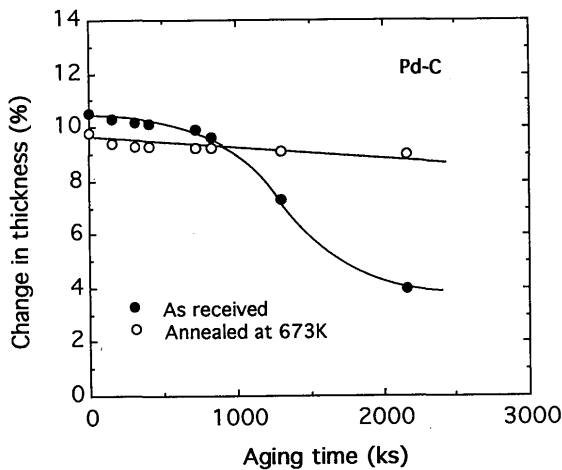
Fig.13 Relation between change in thickness and aging time, as the Pd-C sample was hydrogen-charged and then aged at room temperature.
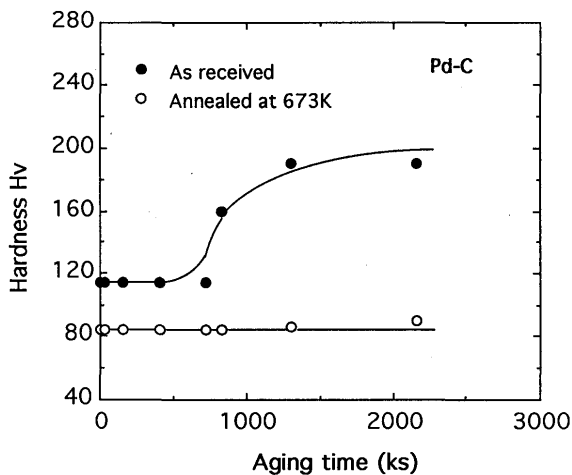

Fig.14 Relation between hardness and aging time as the Pd-C sample was hydrogen-charged and then aged at room temperature.

for 7.2ks, the diffraction peak of β phase only can be observed as shown in (a), however the α and β peaks occurred by aging for 1728ks as shown in (b). The transformation from the α phase to the β phase takes place by aging treatment.

Figure 16 indicates the change in X-ray line profiles as the Pd-C sample annealed at 673K was hydrogen-charged and then aged at room temperature. Before charging, the sample is consisting of α phase. After hydrogen charging, the microstructure is consisting of β phase. However the microstructure keeps consisting of β phase even after prolonged aging.

The sample was vacuum-annealed and dislocation density are little. Consequently, low dislocation density may retard hydrogen evolution from the sample and may
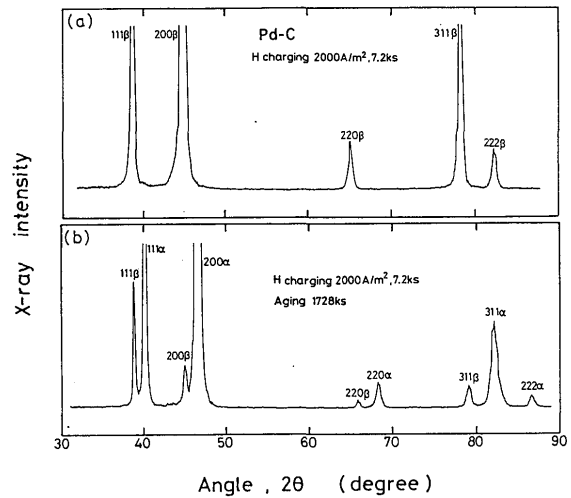

Fig.15 X-ray line profiles as the as-received Pd-C sample was charged and aged at room temperature.

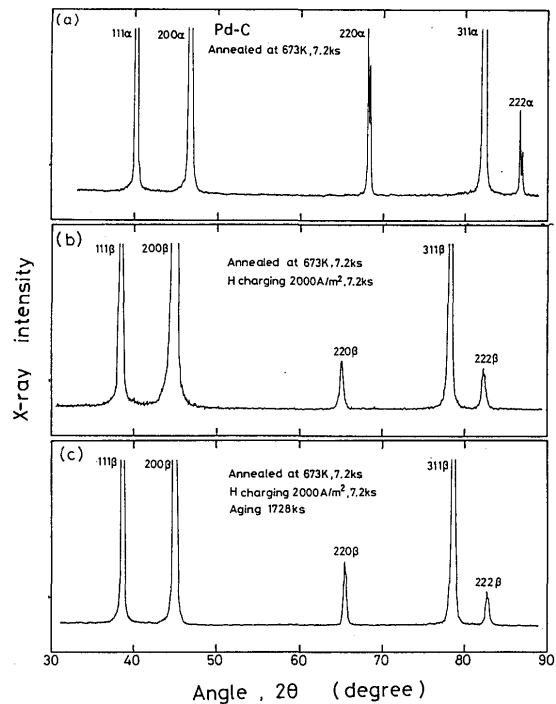**Fig.16** Change in X-ray line profiles as the Pd-C sample annealed at 673K was hydrogen-charged and then aged at room temperature.

retard the transformation from the β phase to the α phase.

Figure 17 indicates the internal friction versus temperature curves as the as-received Pd-C sample was hydrogen-charged and then aged at 1728ks. The peak C and D also increase with increasing aging time. In case
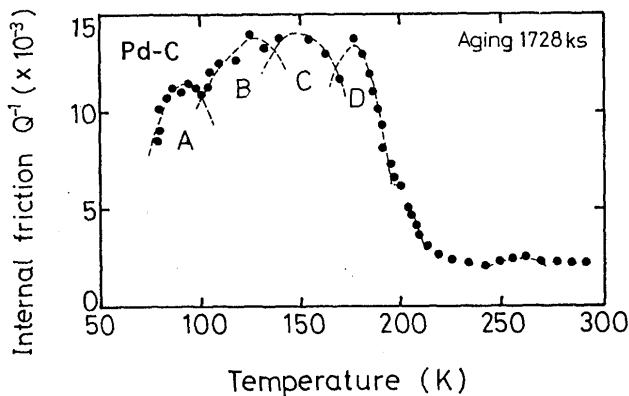
Fig.17 Internal friction versus temperature curves as
the as-received Pd-C sample was hydrogen-
charged and then aged at 1728ks.

of 1728ks aging, hydrogen evolution from the sample is considered to be high, because of the high dislocation density.

As a result, the transformation from the β phase to the α phase occurs more and the interaction of deformation twin and hydrogen is high. Cosequently, peak C and D are considered to be high and hydrogen content seems to be low. The peak profiles are also similar to the curve at 800A/m² shown in Fig.9-(a).

In case of the annealed sample, the internal friction versus temperature curve was hardly changed by aging treatment, because of low dislocation density.

4. Discussion

The palladium-hydrogen phase diagram has been investigated[1]. Palladium readily absorbs hydrogen and forms PdHx. At room temperature, hydrogen is absorbed in the octahedral sites of the face-centered cubic lattice of α phase without much change to the lattice parameter for x <0.015. For higher hydrogen concentration, hydrogen goes into the octahedral site of a larger face-centered cube of β phase that exist from x=0.6 with a lattice parameter of 0.402nm to x=1.0 with a lattice parameter of 0.408nm at a liquid nitrogen temperature. For 0.015 <x<0.6, the system is in the mixed α-β phase region.

The concentration x=1.0 is the limiting value for hydrogen in octahedral sites. There are eight tetrahedral sites per unit cell in the face centered cube. If these sites are occupied, the CaF₂ structure that occurs for a number of dihydrides would be produced. Tetrahedral sites are not occupied in palladium under normal conditions because they are smaller and are closer to each other than the octahedral holes. In a 0.408nm face centered cube, the octahedral sites are 0.28nm apart while the tetrahedral sites are 0.22nm apart.

Recently, Fleischman et al.[5] reported that they observed fusion reactions in palladium cylinders electrolytically charged with deuterium. Jones et al.[6] also observed such reactions in a titanium. Quantum tunneling of a deuterium nucleus to fuse with another nucleus is the most common explanation.

The tunneling probability varies strongly with the distance between deuterium atoms. In a D2 molecule, the deuteriums are 0.074nm apart and the fusion reactions rate is $10^{-74}/d^2$/sec. If the deuteron-deuteron distance is reduced by a factor of 200, this rate increases by about eighty orders of magnitude. This is the basis of muon-catalysed fusion which has been observed. Therefore Fleischman et al.[5] concluded that deuterium atoms have to be less than 0.074nm from each other to account for theirobs ervations. They believe that this is accomplished by the galvanostatic pressure corresponding to the current density during the electrolysis. An overpotential of 0.8V corresponds to a pressure of 10^{26} atmosphere.

If galvanostatic pressure is playing a role in the experiments of Fleischman et al.[5] and Jones et al.[6], we should be able to observe a significant occupation of these tetrahedral sites before multiple occupation of the octahedral sites. In this work, the lattice parameter of α phase is 0.389nm to 0.391nm and that of β phase is 0.4025nm to 0.4045nm by cathodic charging.

Andrews et al.[16] also measured the lattice parameter of palladium electrodes loaded with hydrogen at a current density of 0.25A/cm², and observed that the lattice parameter increases from 0.389nm to 0.408nm after 424.8ks of electrolysis but they did not reported any changes in the lattice structure beyond the β phase[17].

The four internal friction peaks mainly appeared in hydrogenated palladium in this study. The peak A at 80K is related to hydrogen concentration in the α phase or the β phase corresponding Gorsky effect. The peak B at 110K is related to cold work peak with hydrogen and dislocation.

The peaks C and D are new peaks. The peaks C at 150K and D at 170K are considered to be related to the interaction with hydrogen and deformation twin in the α phase and the β phase respectively.

The internal friction peaks were affected by the current density of cathodic charging and this increased with decreasing aluminum impurity in palladium. The current density for cathodic-charging also caused the deformation twin and cracking in the palladium.

The fractofusion model that neutron is evolved from the crack surface as the crack occurred by cathodic charging has proposed. In this study, the formation of cracks depended on the aluminum impurity in palladium

and the model may be confirmed by using palladium with trace aluminum based on the internal friction measurement.

5. Conclusion

The relation between the internal friction peak and hydrogen behavior in palladium was investigated as palladiums containing various aluminum contents were hydrogen-charged at various current densities and aged at room temperature. The results in this investigation are summarized as follows.

(1) The transformation from the α phase to the β phase occurs by hydrogenation and the lattice parameter of α phase increases from 0.389nm to 0.391nm and the lattice parameter of β phase increase from 0.4025nm to 0.4045nm. There was not any changes in the lattice structure beyond α phase and the β phase using X-ray diffraction technique.

(2) The α phase, the β phase, deformation twin and cracks were obesrved in palladium by hydrogenation and aging treatment. The deformation twin and crack increased with decreasing aluminum impurity.

(3) The four internal friction peaks mainly appeared in the palladium. The peak at 80K is related to hydrogen concentration in the α phase or the β phase corresponding Gorsky effect. The peak at 110K is related to cold work peak with hydrogen and dislocation. The new peaks at 150K and at 170K are related to the interaction with hydrogen and deformation twin in the α phase and the β phase respectively.

(4) The internal friction peaks were affected by the current density of cathodic charging and aluminum impurity contained in palladium. The peak at 80K was predominant for the sample with 0.0283mass%

aluminum, the peak at 110K was highest for the sample with 0.01mass% aluminum and the peak at 150K was predominant for the sample with trace aluminum.

(5) The hydrogenation with high current density accelerates the transformation from β phase to α phase during aging at room temperature owing to the high dislocation density.

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