TEM Investigation of Hydrogen Ordering in Pd

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ABSTRACT

TEM was used to study the microstructure of Pd electrodes before and after electrochemical reaction in molten salt and heavy water cells. Hydrogen ordered structure in the non-stoichiometric PH_x was observed in the Pd specimens annealed in air, vacuum and hydrogen furance. On the contrary, high density of dislocations and subgrains and no superlattice structure was observed in the Pd specimens after electrochemical reactions. The reason why no superlattice structure in the electrochemically reacted Pd may be due to traping of hydrogen atoms by defects.

1. Introduction

More than four years ago, thousands of scientists around the world raced to confirmed the claims of electrochemically induced fusion [1,2] especially in the palladium/deuterium system. It is well-known fact that palladium powder at room temperature will absorb hydrogen or deuterium at 1 atm presure to a saturation value which occurs at an atomic ratio H/Pd of about 0.7 which is due to the filling of 4d-band in palladium [3]. Depending on the amount of hydrogen present, x-ray investigation have shown that two different fcc phases exist in the palladium. At low hydrogen concentrations, the α-phase exists and has a lattice constant of 3.89A, very nearly the same as that of pure palladium. However, as the hydrogen concentration is increased, the β-phase (palladium hydride, PH_x) becomes present, in which the lattice is expanded to 4.02A. The hydrogen in the palladium hydride is non-stoichiometric.

Vacancy ordered structures of many non-stoichiometric carbides, nitrides, oxides and silisides of metals [4] were found. However, the vacancy ordered structure in the PdH_x has not been reported yet.

From materials science point of view, the microstructure of the palladium electrode may play a very important role in the case either hydrogen or deuterium

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absorption is crucial [5]. The distribution of hydrogen in PdH_x (order or random) may be a controlling factor for the fusion. It is, therefore, our motivation to carry out the TEM investigation of the microstructure of palladium including the distribution of the absorbed point defects, dislocations and grain structure before and after the electrochemical reactions in order to understand the correlation between microstructure and fusion. Although the electron microscope itself cannot decide the cold fusion issue, the microstructural details at the μm and atomic level might provide a very powerful perspective insofar as the role of microstructures in altering deuterium absorption, concentration, and proximity.

2. Methods

Palladium rods (99.99 %) with a diameter of 4.5 mm were annealed at 1127 K (850 ^oC) in vacuum of 10^{-2} torr and in air for two hours. Some of annealed palladium rods were then electro-polished with a mixture of 33% (wt%) sulphuric acid, 33% orthophoshorric acid and 34% nitric acid before they were put into electrochemical cells for fusion experiments. Two different fusion cells were used our experiments: 1) the molten salt cell contains Pd anode and Al cathode. The molten salt electrolyte is a eutectic mixture of 113.3 g KCl and 122.3 LiCl. Temperature of this cells was kept at 450 ^oC. 2) second type of cell is composed of heavy water electrolyte, Pd cathode and Pt anode. The heavy water electrolyte is 0.1 M LiOD in D_2O. The temperature of this cell was kept at the room temperature.

The annealed and electrochemically reacted palladium rods were cut into pieces of about 1 to 2 mm thick and punched into discs a diameter of 3 mm. The specimens were then mechanically thinned to about 20 μm. Specimens were dimpled until a small hole appears in the center of disc. A copper mesh was bonded to the sample by epoxy . The sepecimens were finally thined by ion milling for about 4 hours before examination of TEM.

TEM experiment were carried out by using JEOL 200CX and 4000EX microscopes. The MULTI-SLICE program written by Roar Kilaas was used to simulate the diffraction patterns [6].

3. Results and Discussion

We have observed weak superlattice diffraction spots in the annealed Pd specimen (in air, vacuum and hydrogen furance) in many crystallographic zone axes such as [111], [112], [221] and [332] diffraction patterns. The first two diffraction patterns are depicted in the figures 1 (a) to (b) and the superlattice diffraction spots are indicated by arrows. On the contrary, no superlattice diffraction observed in the electrochemically reacted Pd specimens which contain high density of dislocations and subgrains.

We have investigated many possibilities for the origin of these superlattice diffraction spots such as surface incomplete cell, surface reconstruction and hydrogen vacancy ordering in PH_x. Ultra-high vacuum and very thin specimen are required for the superlattice diffraction due to surface effect being able to be observed. We have found the superlattice diffraction in rather thick area of Pd specimen which was not

observed in the ultrahigh vacuum.

There may have little amount of PH_x in the annealed Pd specimen. The hydrogen in the non-stoichiometric PH_x may form order structure like many non-stoichiometric carbide, nitride, oxide and siliside of metals [4]. The hydrogen ordered structures viewing from [111], [112] are given in the figures 2 (a) to (b) and their corresponding computed diffraction patterns are depicted in the figures 3 (a) to (b) which have very good matches with the experimental diffraction patterns in the figures 1 (a) to (b), respectively.

Since the electrochemically reacted Pd specimens contain high density of dislocations and subgrains which may trap the hydrogen/deuterium atoms so that the hydrogen/deuterium atoms may not allowed to diffuse into the Pd lattice to form ordered structure. This may be the reason why we do not observe the superlattice diffraction spots in the electrochemically reacted specimens.

5. Conclusions

Hydrogen atoms were found to form ordered structure in the Pd specimens which were annealed in the air, vacuum and hydrogen furance. On the contrary, no hydrogen ordered structure can be found in the Pd specimens which were electrochemically reacted in the motlen salt and heavy water cells.

6. References

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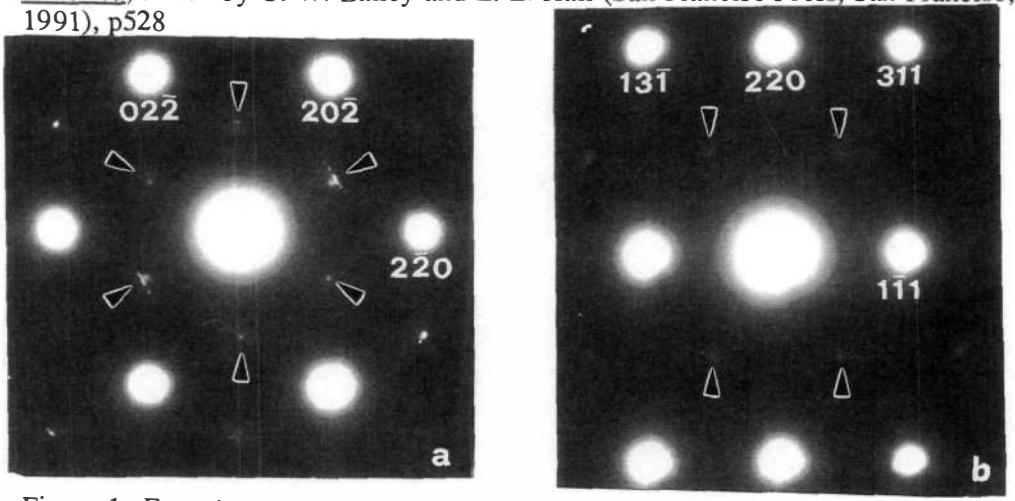

Figure 1. Experimental diffraction patterns of a) [111] zone axis and b) zone axis [112]

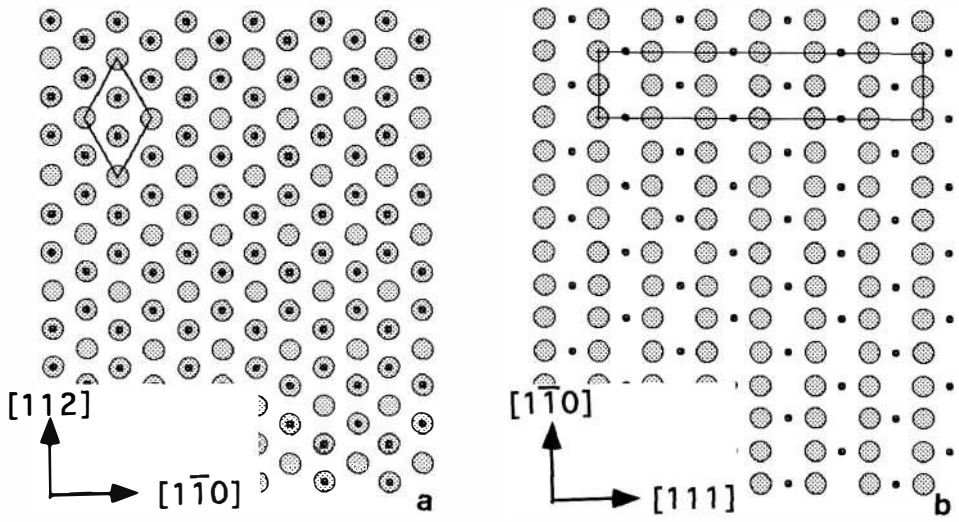

Figure 2. Hydrogen ordered structures viewing along a) [111] direction and b) [112] direction

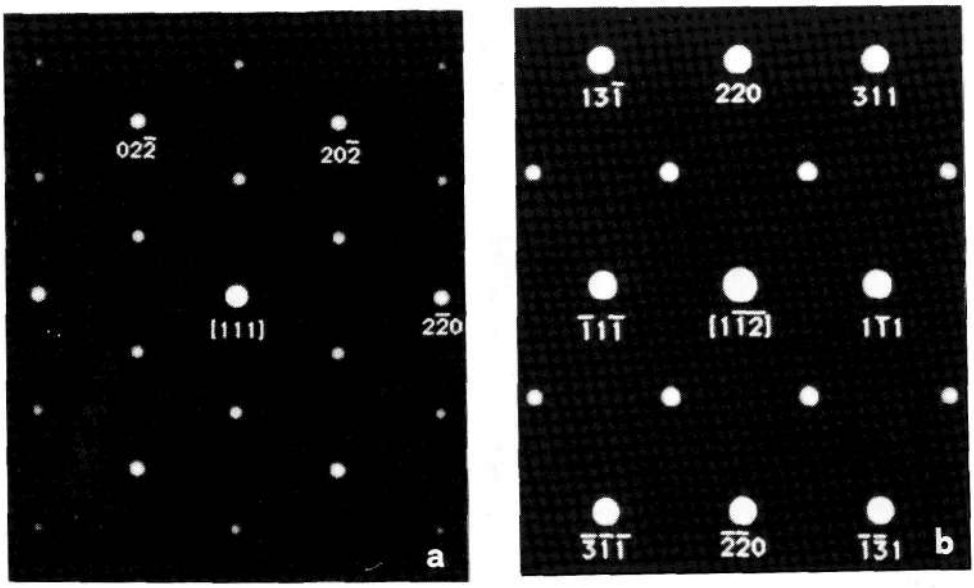

Figure 3. Computer simulated diffraction patterns of a) [111] zone axis and b) [112] zone axis for the projected structures shown in the figures 2