Application Note

Atmosphere™

Visualizing Hydrogen Absorption in Palladium Thin Films using *In Situ* Environmental TEM

Introduction

Hydrogen as a chemical fuel is an environmentally friendly energy source and is considered by many the fuel of the future. It is currently used in systems such as fuel cells for electricity generation and in internal combustion engines. In both cases, the chemical reaction product is only heat and water. Although promising, there are two primary barriers to widespread adoption of this clean energy source. The first barrier is creating the fuel itself, which is usually produced from water via a chemical splitting reaction. A variety of reaction methods have been demonstrated, but to date all take significant energy and resources. The second barrier to widespread commercialization is storage. Hydrogen (H_2) is a light molecule and can seep out of pipes and holding tanks over time, making long term storage problematic. Research and engineering groups around the world are investigating several potential hydrogen storage materials and strategies. Hydrogen storage in certain metals, palladium in particular, is one promising material being studied by scientists.

It has long been known that palladium can absorb hydrogen effectively at moderate temperatures and pressures. Hydrogen occupies interstitial sites in the Pd fcc lattice. At low absorbed concentrations of hydrogen, the Pd lattice slightly expands, however, above a concentration threshold of around 2%, the lattice expands further to accommodate increased proportion of hydrogen. The Pd alpha phase and beta phase, called palladium hydride, are used to describe the Pd/H structure under low and high concentrations, respectively. When transitioning into the beta phase, the expansion can be detected via diffraction and measuring subtle changes in the lattice spacing. The process is reversible and the lattice contraction can also be measured when Pd returns to the alpha phase.

Bulk *in situ* measurements, such as X-ray diffraction, can detect these changes in the lattice spacing of palladium, however bulk techniques do not provide direct visual information at the nano and atomic scale. Subtle changes in the microstructure, such as grain growth in thin films and particle coalescence in nanoparticles, which both could affect the storage behavior of the material, cannot be directly visualized, so analyzing material changes at the nano-scale as a result of heat and hydrogen pressure can be challenging. TEM is one of the best ways to directly image materials at small length scales, and it provides a means to analyze samples using diffraction and element identification with EDS and EELS, which is particularly important when working with materials such as palladium alloys. The TEM requires high vacuum to operate, however, and is generally not amiable to high pressures without major modifications to the instrument. With the introduction of the Protochips Atmosphere™ Gas E-cell system, researchers can now expose samples to gas environments and temperatures that mimic real-world conditions, including the conditions required to create palladium hydride. Using Atmosphere with new and existing TEMs, researchers can visualize atomic scale processes in real time, so more relevant information can be obtained from experiments with minimal additional effort.

Experiment

Researchers in the Materials Science department at the University of Manchester performed *in situ* hydrogen absorption experiments on a thin film of Pd. The Pd sample was deposited directly onto a temperature-controlled support called a thermal E-chip. The E-chip has a thin, ceramic heating membrane, which is actively controlled with the Atmosphere software to automatically adjust the temperature under different gas species and pressures (up to 1 atm). The Pd was deposited on the heating membrane by sputtering through a shadow mask with a thin slit directly above the membrane to localize the deposition in the region of observation. A second window E-chip with a SiN membrane sits on top of the thermal E-chip in the TEM holder creating a thin gas cavity sealed with small o-rings preserving the high vacuum of the TEM column. During the experiment the sample was imaged under 1 atm (760 Torr) of H_2 at temperatures between 200 °C and 300 °C. An FEI Titan, Cs probe corrected, in the University of Manchester's Materials Performance Centre was used and operated in STEM mode at 200 kV.

Discussion

The lattice expansion resulting from the formation of the beta phase can be detected using electron diffraction in the TEM. For this experiment a diffraction pattern was taken while the Atmopshere cell was held at 20 Torr of H_2 at 200 °C, and a second pattern was taken during exposure to 1 atm of H_2 at 300 °C. The two patterns were then compared. Note this sample was a thin

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polycrystalline Pd film, and as a result formed diffraction rings, due to multiple orientations of small crystalline grains in the sample. A one dimensional line scan showing the intensity of the diffraction rings on each pattern is displayed in Figure 1. The lattice expansion is immediately apparent, and spacings can easily be extracted using this graph, which are shown in Table 1. The lattice parameter for metallic Pd is 0.389 nm, and the measurements taken from each reflection in the diffraction pattern closely match this value within a small margin of error. The lattice parameter for palladium hydride is 0.4025 nm, and the measured values taken during hydrogen exposure, are also close to this value. To correlate physical changes in the microstructure, high-resolution images of the Pd lattice can be taken. One such image is shown in Figure 2, which was taken under 1 atm of H_2 at 300 °C.

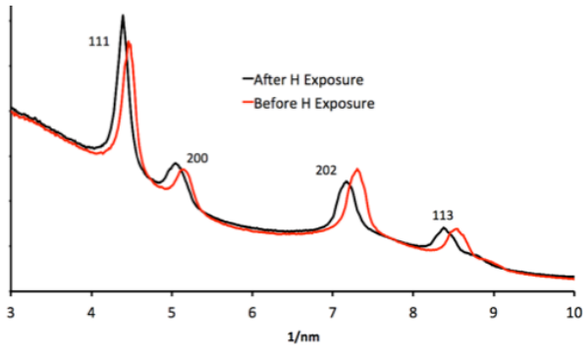

Figure 1: One dimensional line scans of before and after powder diffraction patterns. After exposure to hydrogen at elevated temperatures (black line), the lattice expands to accommodate it.

Reflection	Before H absorption Lattice spacing (nm)	Lattice Parameter (pure Pd - 0.389nm)	After H absorption Lattice Spacing (nm)	Lattice Parameter (beta phase - 0.4025)
111	0.223	0.386	0.228	0.395
002	0.195	0.39	0.199	0.398
202	0.137	0.387	0.14	0.396
113	0.117	0.388	0.119	0.394

Table 1: Lattice spacings measured from the diffraction pattern showing the difference in inter planar spacing before and after hydrogen absorption.

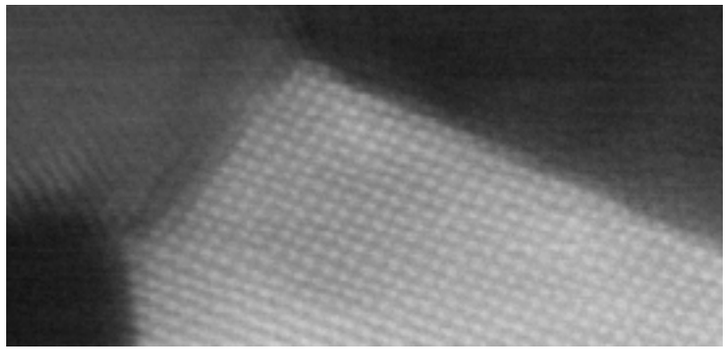

Figure 2: High resolution HAADF STEM image of a Pd grain during exposure to 1 atm of H_2 at 300 °C. Scale bar is 2 nm.

Applications

Palladium and palladium alloys have the potential to provide an effective solution to the hydrogen storage problem in several key applications, but to fully understand how the material behaves under specific environmental conditions further study is needed. The TEM can play a crucial role in characterizing the behavior of palladium and palladium alloys during systematic exposure to hydrogen at specific temperature and pressures. By adding the Protochips Atmosphere Gas E-cell system to your TEM, exposing samples to particular gas species and to applying accurate temperatures over a wide pressure range is now routine. Atmosphere preserves the resolution and analysis capabilities of the most powerful TEMs on the market today. Since it is a holder-based system, Atmosphere is compatible with most modern TEMs, and can be added to new and existing instruments with no special modifications whatsoever. Contact us to discuss the full range of capabilities of the Atmosphere E-cell System for your applications. We can be reached at (919) 377-0800 or contact@protochips.com.

Reference:
Images and data courtesy Prof Sarah Haigh and Eric Prestat, University of Manchester; Tadahiro Yokosawa, Karlsruhe Institute of Technology

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