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In situ X-ray diffraction analysis of the Pd–H system at high pressure

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Abstract

In the present work palladium thin foils have been hydrogenated at high pressure. In situ monochromatic X-ray diffraction performed under 5 GPa of hydrogen pressure has allowed to follow the formation of hydrogen-rich Pd–H phases as well as the presence of ordered superabundant vacancy phases. The occurrence of hydrogen-rich Pd–H phases as well as the presence of ordered superabundant-vacancy phase is discussed. Sme discrepancies with the early experiments of Fukai are observed. In particular, our results suggest the occurrence of a superstoichiometric defect hydride related to the γ' phase. A structural model is proposed and needs to be confirmed by using neutron diffraction.

Keywords: Pd; High pressure; Hydrogen effect; Superabundant-vacancy

1. Introduction

Hydrogen may be reversibly inserted at normal pressure and ambient temperature in many intermetallic compounds leading to interstitial compounds (hydrides) whose structural, chemical and physical properties are strongly modified upon hydrogen insertion. It is also known that other hydrogenated phases may be produced using high-pressure hydrogenation. An interesting case is that of hydrogen-induced vacancy phases for which hydrogen desorption is accompanied by a reconstruction of the starting network. Since the pioneering work of Fukai and Okuma [1] who discovered that vacancies could be produced in the palladium metal lattice by using high-pressure hydrogenation, we have been able to reproduce these results and stabilize superabundant vacancy phase at room temperature and normal pressure [2]. However, it has been known for a long time that this is not the only way to produce vacancy phases and, in this respect, ion implantation-based techniques are particularly suitable [3–5]. So far, our investigations have confirmed that the use of high-hydrogen pressures was a successful route to produce hydrogen-induced vacancy-phases similar or not to published work. Although the structural and physical properties of these end-phases have been accounted for; a clue for understanding the phase formation can be obtained in the course of in situ diffraction experiments. So far, such experiments have been carried out using energy-dispersive diffraction set ups. In this paper we have followed the in situ high-pressure hydrogenation of palladium at 5 GPa from room temperature up to 800 °C using monochromatic X-ray diffraction.

2. Experimental details

Samples of pure palladium foils that had been cold-rolled down to the thickness of 0.10 mm were cut into disks (1 mm in diameter) in order to fit the size of the laboratory-made high-pressure cell. They were subsequently encapsulated together with an internal hydrogen source in a NaCl container impervious to hydrogen. The high-hydrogen pressure was applied using the so-called Paris–Edinburgh press the description of which can be found in Ref. [6]. The hydrogen provider was a pellet of $C_{10}H_8$. When heated it decomposes irreversibly

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and supplies free hydrogen that can react with the sample. The palladium foil and $C_{10}H_8$ were separated by a BN disk (0.1 mm in thickness) in order to prevent from possible carbon diffusion. The press together with the high-pressure cell were installed at ESRF. Two dimensional X-ray diffraction patterns were taken in transmission geometry on the ID30 beamline at ESRF operated at the wavelength of 0.1581 Å. The images collected from the image-plate detector were integrated using the FIT2D program in order to obtain conventional X-ray diffraction patterns.

The first stage of the experiment was compression, the pressure was raised up to 5 GPa, followed by the temperature increase where the sample was heated up to 800 °C and maintained there for approximately 8 h. The X-ray diffraction patterns were collected sequentially every 30 °C. More details about the whole experimental set up (HP cell, pressure transmitter, pressure calibration, X-ray detector) can be found at ESRF web site.

3. Results and discussion

At a constant pressure of 5 GPa and in the course of heating from 20 up to 800 °C the main phase appears to be metallic palladium with a lattice parameter that varies from 3.868(4) to 3.892(5) Å (under compression). This is shown on the 3D plot of diffraction patterns during the heating slope in Fig. 1. At this stage, it is important to mention the differences between the current study and the early results of Fukai and Okuma [7]. Both experiments were carried out using rather similar experimental procedures. In the Fukai and Okuma results, at 5 GPa of hydrogen lattice parameter of Pd increased from about 3.85 Å at 25 °C to about 4.1 Å at 700 °C linearly and then it reduced to 4.06 Å because of vacancy formation. The pressure of the present work is the same but the lattice parameter change is significantly different in the temperature range between 25 and 800 °C. From our values, an attempt to discuss vacancy formation in the main phase can be made. The vacancy concentration can be calculated using the formula used by Fukai in [1] and it leads to 3.6(9)%; this is the first discrepancy. Another one lies in the occurrence of different diffraction lines.

Starting from 350 °C new diffraction lines are detected and those are present up to 510 °C as seen in Fig. 2. At the temperature of 550 °C these lines are much weaker but still present on the diffraction pattern as shown in Fig. 3. The set of new lines amounts 7 in total in the 2Θ angular range and could be satisfactorily accounted for using the tetragonal cell: $a = 3.034$ Å, $c = 6.170$ Å. The volume of this tetragonal cell is 57 Å^3 and it ranges below the unit-cell volumes of metallic Pd and fcc β-hydride (59 and 66 Å^3, respectively). This value of the unit-cell volume actually roughly corresponds to the double of the volume found [8] for a hydride of palladium formed when bombarding palladium films with protons and cooling in an atmosphere of hydrogen. When looking at the cell parameters it can be seen, that the proposed cell corresponds to a superstructure of the so-called γ′ phase [8], this latter phase being a form of superstoichiometric hydride observed in a thin film. A distinguishing feature of the γ′ phase is the presence of 25% of vacancies in the metal sublattice. In our case, the doubling of the *c* parameter lead us to suspect a vacancy ordering. A model with half less vacancies than for the γ′ phase was assumed and refined with a fair agreement (Fig. 4). Note that in this preliminary model we are not able to unambiguously locate hydrogen. Actually refinements in which hydrogen was introduced statistically distributed lead to the same kind of agreement factors that refinements with no hydrogen at all; this can be easily understood since X-rays

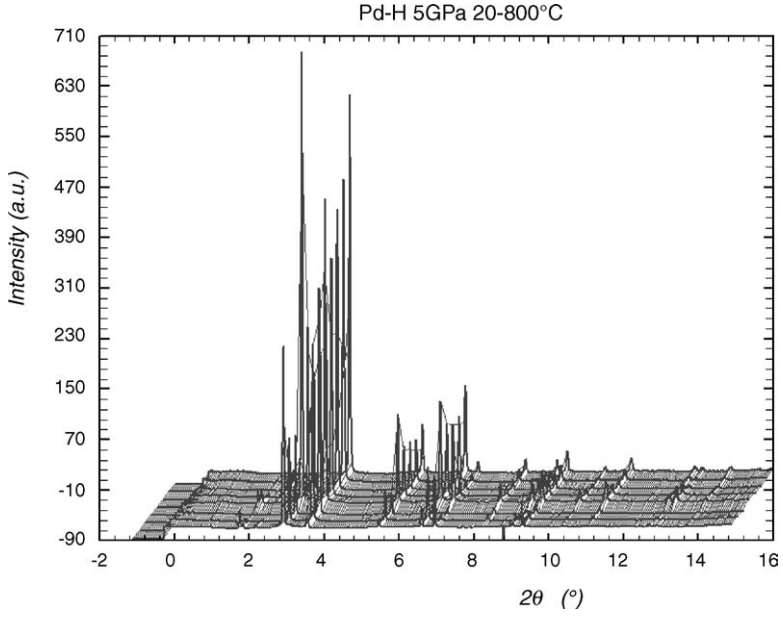

Fig. 1. Evolution of the X-ray diffraction patterns under compression from 20 °C (bottom) to 800 °C (top).

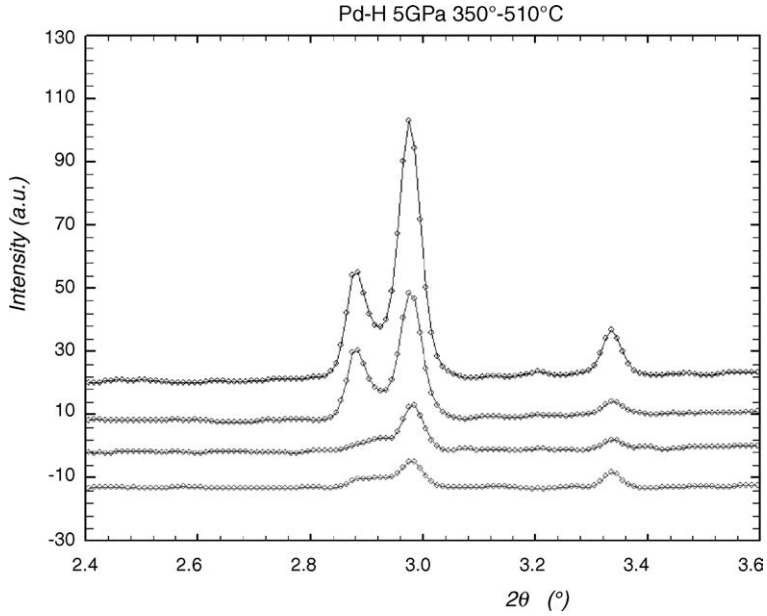

Fig. 2. Detail of the X-ray diffraction pattern showing the growth of the tetragonal phase. The temperatures are 350, 410, 450 and 510 °C from bottom to top.

are not sensitive to hydrogen due to its too low scattering factor with respect to the metal matrix. So far, in the light of these preliminary results it is assumed that this new tetragonal phase is a defect hydride structure. We rely on the following experimental facts:

- The presence of vacancies (12.5%) is known to make the formation of defect hydride structures probable.
- For this experiment we used $C_{10}H_8$ instead of $C_{14}H_{10}$ used in our previous experiments, $C_{10}H_8$ decomposes (under normal pressure) at lower temperatures than $C_{14}H_{10}$, it is then sure that hydrogen is released at 350 °C.
- The X-ray diffraction mode for this experiment was the true Debye–Scherrer geometry, then the intensities of diffraction lines are not biased and can be used as such (after the usual corrections) for a structural analysis. This is not always true in the energy-dispersive mode.

As can be seen from Figs. 1 and 2, this tetragonal phase is merely distinguishable at temperatures higher than 550 °C;

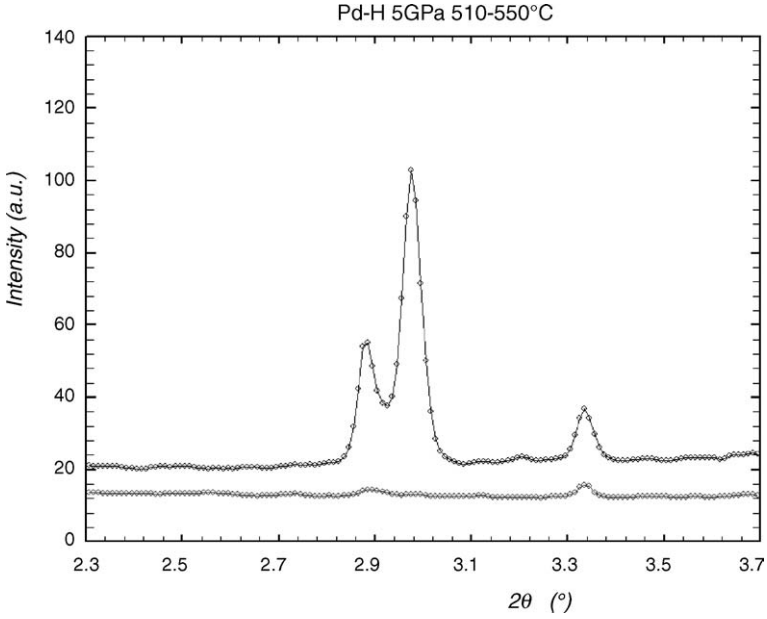

Fig. 3. Fading of the tetragonal phase (detail). The patterns were recorded at 510 °C (up) and 550 °C (down).

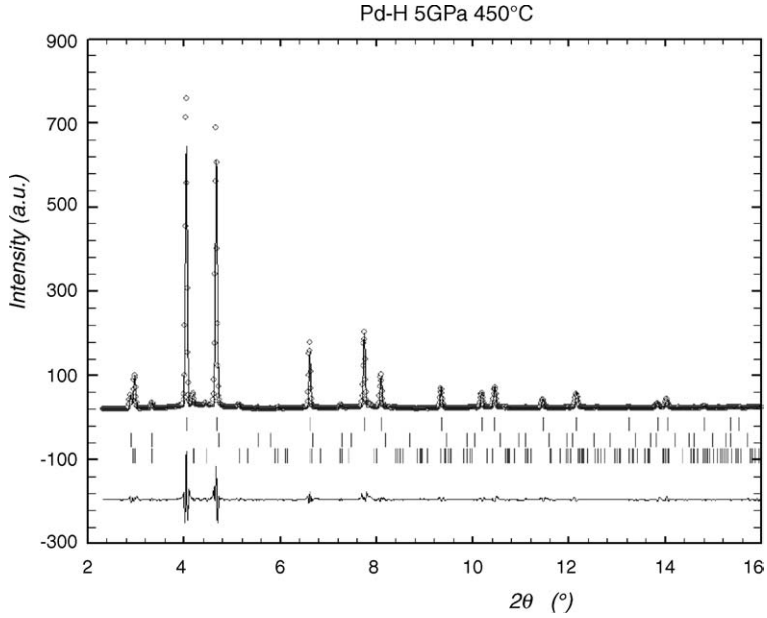

Fig. 4. Full pattern Rietveld refinement at 450 °C. The line markers respectively refer to Pd, NaCl and to the tetragonal phase from top to bottom.

then at 800 °C extra lines are again significantly present and can be accounted for by using the cubic unit cell of the γ′ phase with $a = 3.056$ Å. A satisfactory refinement could be performed for this latter structure (Fig. 5). We are here presumably dealing with a high-temperature modification of the same hydride with a statistical distribution of vacancies and henceforth of hydrogen atoms. In this respect a neutron diffraction investigation is highly needed. In the current state of observations, X-ray diffraction did not detect a first order transformation, and, the tetragonal phase appears to be metastable. It is important to note that although this tetragonal phase is a minor phase and its proportion amounts circa 4 vol.% (assuming homogeneous pressure and 12.5% metal vacancies), its occurrence brings support to the concept of hydrogen-induced lattice migration.

Another interesting feature of this experiment is the detection of a recrystallization process for palladium that starts at 600 °C under compression of 5 GPa. This process could be clearly seen on the image plate where the Debye–Scherrer rings transformed into dotted irregular lines. A careful line shape analysis is in progress as well as the study of the temporal variation of the lattice parameter at 800 °C. Unfortunately no information is available for the cooling down due to an explosion of the cell.

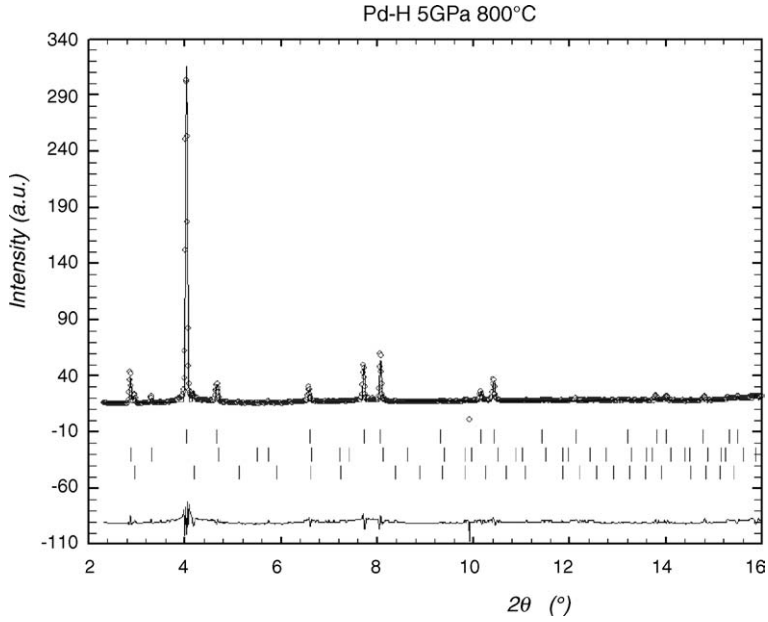

Fig. 5. Full pattern Rietveld refinement at 800 °C. The line markers respectively refer to Pd, NaCl and to the γ′ phase from top to bottom.

4. Conclusion

These experimental observations prompt us to suggest that a new version of superstoichiometric defect hydride strongly related to the γ' phase has been detected in the course of this in situ experiment, followed by the conversion to the parent phase at high temperature (800 °C). We have brought an additional piece of evidence to Fukai's expectations stating that, as long as interstitial hydrogen exists in the lattice at temperatures where metal-atom vacancies can migrate, vacancy concentrations as high as 25% (that is well above the thermal equilibrium value) can be reached.

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