Experimental report

11/02/2019

Proposal: **5-25-260** **Council:** 4/2017

Title: Kinetic study of phase transformations in the deuterated Pd/Ag alloy

Research area: Materials

This proposal is a new proposal

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Samples: $Pd_{0.77}Ag_{0.23}D_x$

Instrument	Requested days	Allocated days	From	To
D20	2	2	19/03/2018	21/03/2018

Abstract:

Hydrogen selective palladium membranes are important for technological processes of H separation and purification, but they become brittle because of repeated alpha - beta phase transformations. Pd is usually alloyed with Ag to avoid this membrane embrittlement, assuming a single-phase behaviour during hydrogenation. However, in the previous experiment 5-25-247 on D2B, in-situ measurements on $Pd_{0.77}Ag_{0.23}D_x$ at variable T and p(D_2) revealed a transformation between two FCC phases with different lattice constants and deuterium contents, depending on time and high-pressure pre-treatments. The D-poorer phase seems to be metastable and to transform progressively into the D-richer one. An experiment is thus proposed on the high-resolution high-intensity D20 diffractometer, with the aim of studying the kinetics of this process. Two days are requested, to collect series of 20 consecutive patterns at 80 and 160 °C, and pressures in the 1 to 12 bar range, including the study of baric history effects.

Report on experiment 5-25-260: D20; 19/3/2018 - 21/3/2018

‘Kinetic study of phase transformations in the deuterated Pd/Ag alloy’

Experimental details

Neutron diffraction measurements by D20 were carried out in the 1-153° 2θ range at λ= 1.5420 Å on a 0.05 mm thick foil of $Pd_{0.77}Ag_{0.23}$ alloy, rolled up inside the sample holder. This was an Al can provided with a heating system and connected to a gas manifold, which allowed the holder to be evacuated and filled with deuterium at variable pressure. A diffraction pattern with the features of pure aluminium was recorded on the empty cell, for calibration purpose of subsequent measurements.

Kinetic measurements of the absorption of D_2 into the $Pd_{772}Ag_{228}$ alloy were performed in isothermal conditions at 80, 150 and 200 °C. On heating the sample in vacuum the appropriate temperature was attained, and after a 30 min stabilization time deuterium gas was let in and three subsequent kinetic cycles at $p(D_2)$ = 1, 4 and 8 bar were carried out. Then the sample was evacuated and heated to the next T value, repeating the three cycles at different pressures. Each cycle was made up of consecutive collections of diffraction patterns (measurement time: 10 min for 80 °C, 1 and 4 bar; 5 min in all other cases), till no changes appeared in the diffractograms so that the absorption process could be considered to be completed. At the cycle end a final pattern was measured for 15 min. The three temperatures were attained consecutively on heating, and not separately on cooling from 200 °C as in the previous experiments on D1B[1] and D2B.[2] This procedure was chosen to save time for the long kinetic measurements, because cooling is very time-consuming. On the other hand, in the D2B experiment the sample was heated in vacuum to 200 °C, it was filled with D_2 at 1 bar, and then it was cooled to 80 °C at constant pressure, collecting diffraction patterns during deuteration due to cooling. Then the alloy was evacuated and heated again to 200 °C, it was filled with D_2 at 4 bar, it was evacuated, filled with D_2 at 1 bar, and cooled to 80 °C at constant pressure, again collecting diffraction patterns on deuteration subsequent to cooling.

All collected patterns were analyzed by the FullProf computer package, including one or two Rietveld-refined phases of FCC $Pd_{0.772}Ag_{0.228}D_x$, and aluminium from sample-holder as additional phase (LeBail-like profile fitting). For Al, only the unit-cell constant was refined in each pattern, keeping fixed the other Al parameters obtained from the calibration file. As for $Pd_{0.77}Ag_{0.23}D_x$, the unit-cell edge, the occupation factor of D (located on the *Fm*-3*m* octahedral site), the displacement factors of D and of Pd/Ag, the scale factor and the U, V, W, Y profile parameters were always refined.

Results and discussion

At the end of each kinetic cycle, when equilibrium of the deuteration reaction was attained, a single FCC phase of $Pd_{0.772}Ag_{0.228}D_y$ was detected in the patterns. The results of the corresponding Rietveld refinements are reported in the Table below.

The deuterium occupancies ν appear to be slightly lower than the values considered to be at equilibrium (at the same temperatures) in our previous study.[1] This may be related to the different thermal cycle adopted in the present case for saving time in the extensive kinetic measurements.

T (°C)	*p*(D_2) (bar)	R_p (%)	wR_p (%)	R_B (%)	*a* (Å)	o.f.(D) = *ν*	*B*(Pd) (Å^2)	*B*(D) (Å^2)
80	10^{-6}	8.4	12.6	6.3	3.93153(3)	0	0.88(2)	----
80	1	6.3	9.3	2.8	4.01650(3)	0.326(7)	1.08(3)	4.4(1)
80	4	6.1	9.2	2.0	4.02171(3)	0.363(8)	1.28(3)	5.4(2)
80	8	5.5	8.4	2.1	4.02465(3)	0.371(7)	1.32(3)	5.2(1)
150	1	6.4	10.0	3.1	3.99836(3)	0.199(7)	1.06(3)	3.5(2)
150	4	6.0	9.4	3.2	4.01527(3)	0.240(8)	0.92(3)	3.5(2)
150	8	5.8	9.2	2.7	4.02030(3)	0.262(7)	0.98(3)	3.8(2)
200	1	6.7	11.1	2.8	3.96753(3)	0.079(5)	1.30(3)	1.2(4)
200	4	6.1	9.8	3.4	4.00381(3)	0.190(7)	1.13(3)	3.5(2)
200	8	5.6	9.1	2.6	4.01342(3)	0.221(7)	1.08(3)	3.9(2)

The results of kinetic measurements vs. time are different according to different temperature and pressure conditions. At T < 200 °C and p(D2) = 1 bar the FCC Bragg peaks of the sample appear to be split (Fig. 1), and with increasing time the intensity ratio of each pair varies continuously in favour of the peak at lower 2*θ*.

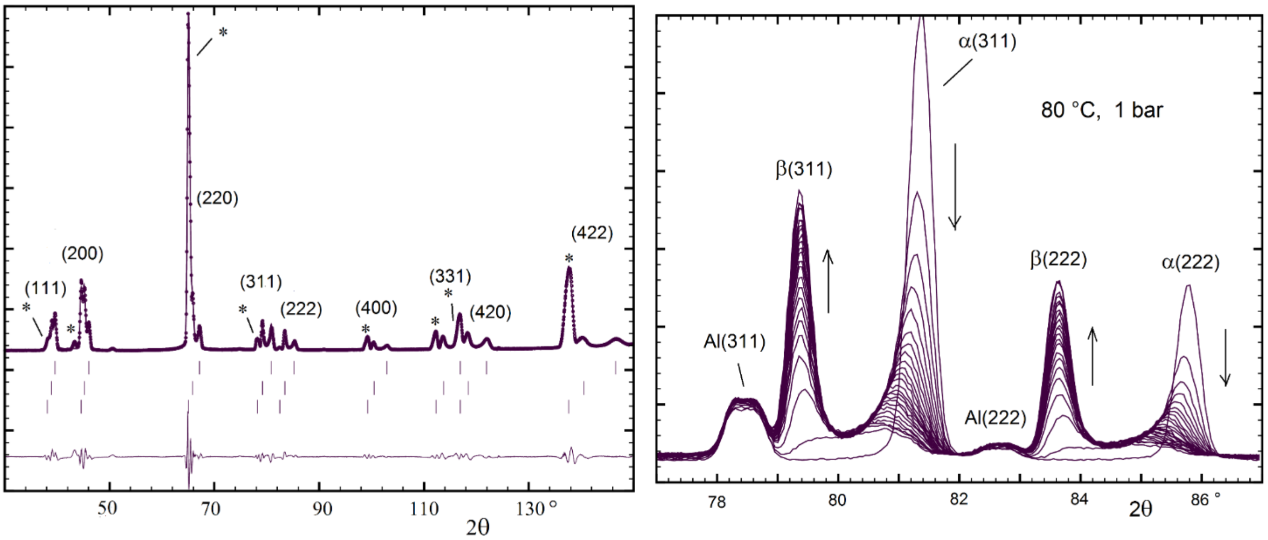

Fig. 1. Diffraction pattern of two-phase (α+β) $Pd_{0.772}Ag_{0.228}D_ν$ during deuterium absorption at *T* = 80 °C, *p*(D_2) = 1 bar. Vertical bars denote the Bragg peak positions for the α and β phases (upper and middle rows), and for Al of the pressure cell (lowest row, also emphasized by asterisks). Right-hand picture: isothermal α → β phase transformation of $Pd_{0.772}Ag_{0.228}D_ν$ during deuteration progress; arrows indicate the direction of increasing time.

The splitting indicates that two cubic phases are present, to be identified with the α and β modifications of palladium hydride. This result is fully consistent with what suggested by the preliminary experiment on D2B.[2] Rietveld refinements provided the values of the corresponding a_α and a_β lattice constants, ν_α and ν_β occupancies of D, and of the β phase volume fraction vs. time during deuteration progress. A continuous α → β transformation takes place till reaction end. At T = 200 °C or p > 1 bar a single phase was always observed. The phase diagram of $Pd_{0.772}Ag_{0.228}D_\nu$ is thus shown to present a α+β two-phase domain less extended but similar to that of PdH_ν.

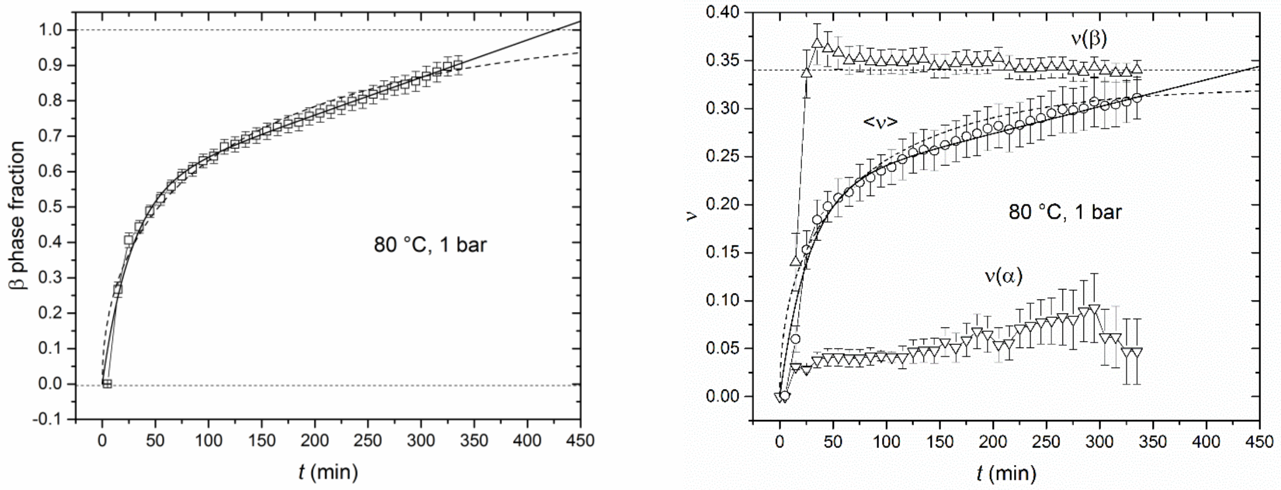

Fig. 2. Volume β phase fraction from Rietveld refinements of $Pd_{0.772}Ag_{0.228}D_\nu$ during the progressive isothermal D_2 absorption at 80 °C, 1 bar. Right-hand picture: occupancy ν of deuterium D in each of the α and β phases and weighted average <ν> against D_2 absorption time.

Some kinetic results are shown in Fig. 2, where the β phase fraction and the deuterium occupancies obtained from Rietveld refinements at 80 °C, 1 bar are plotted vs. time. The mechanism of reaction includes two steps. The second step, following a zero-order kinetics, corresponds to adsorption and dissociation of deuterium gas on the sample surface; it becomes rate-determining after that first-order nucleation of the hydride phase in the bulk (first step) has come to end. The thick full lines represent the functions corresponding to such kinetic models, to which data were fitted.

(1) Catti M., Fabelo O., Filabozzi A., Pietropaolo A., Tosti S., Pozio A., Santucci A. Neutron diffraction study of the $Pd_{0.772}Ag_{0.228}D_\nu$ membrane for hydrogen separation. *Int. J. Hydrogen Energy* **2017**, *42*, 6787-6792.

(2) https://doi.ill.fr/10.5291/ILL-DATA.5-25-247