Experimental report

07/02/2017

Proposal: 5-25-247 **Council:** 4/2016

Title: Neutron diffraction measurements on deuterated Pd/Ag alloy

Research area: Materials

This proposal is a continuation of 5-25-241

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Samples: Pd0.77Ag0.23Dx

Instrument	Requested days	Allocated days	From	To
D2B	3	2	23/11/2016	25/11/2016
D20	2	0		

Abstract:

Hydrogen selective palladium membranes are important for technological processes of H separation and purification; Pd is usually alloyed with Ag to avoid membrane embrittlement. The electrical resistivity of a Pd100-yAgy alloy shows an unusual behaviour vs. T on hydrogenation, with a puzzling minimum around 150 °C; this was claimed to depend on a variable distribution of H atoms among different structural sites. Hence the interest of structural studies by neutron diffraction. In the previous measurements on D1B (exp. 5-25-41), data were collected at low resolution on Pd0.77Ag0.23Dx at variable T and p(D2). D is found to be located mostly on octahedral sites, but some uncertainty about possible occupation of secondary sites remains. A continuation of the experiment is proposed on the high-resolution high-intensity D20 diffractometer (with D2B as possible alternative), with the aims of (i) definitely detecting possible D location in non-octahedral sites, (ii) confirming the S-shaped behaviour of D occupancy vs. T, found at 1 bar, also at higher pressure, and (iii) checking the dependence of D uptake on pressure.

Preliminary report for experiment 5-25-247 D2B; 23/11/2016 - 25/11/2016
'Neutron diffraction measurements on deuterated Pd/Ag alloy'

Experimental details

Neutron diffraction measurements by D2B were carried out in the 1-160° 2θ range at λ= 1.5942 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.

After measuring the pattern of the sample in vacuum at 196 °C, 12 full data sets were collected at different temperatures and pressures: $p(D_2)$=1, 2, 4 bar and T = 241, 196, and 78 °C. In most cases the measurement time was 2.7 h. Between subsequent runs the temperature and/or pressure was changed, and then a waiting time of 0.5 h was allowed before data collection. In some cases intermediate evacuation was performed as well.

Results and discussion

All collected patterns were analyzed by the FullProf computer package, including two phases in the refinement: the FCC $Pd_{0.772}Ag_{0.228}D_x$ deuterated alloy (Rietveld refinement), and FCC aluminium (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.

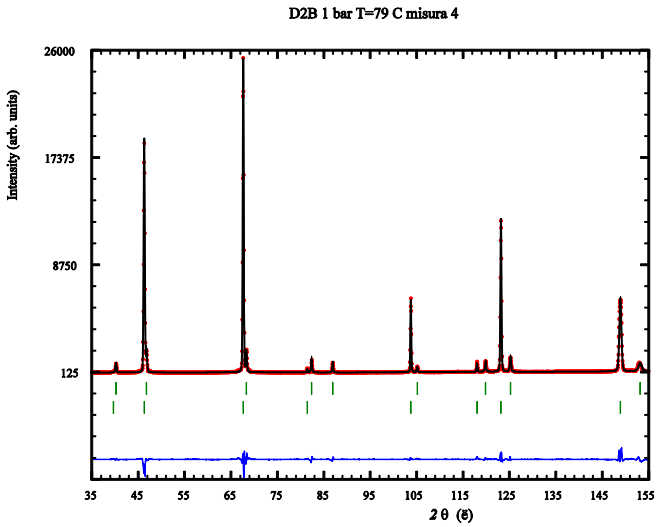

Fig. 1. Rietveld observed, calculated and difference intensity profiles for diffraction pattern n. 13, recorded at 79 °C and 1 bar after pre-treatment at 4 bar. Upper and lower ticks denote Bragg peaks of the sample and of the Al cell, respectively.

The pattern of the last collected data (n. 13, cf. Table 1) is displayed in Fig. 1, showing a much better resolution with respect to the previous experiment on D1B (5-25-241). Now all overlapping between peaks from the sample and from the Al cell is well resolved. The refined structural parameters are reported in Table 1 for all collected patterns. The FCC structural model has Pd-Ag disordered at x = 0, y = 0, z = 0, and D with variable occupancy on the octahedral site at x = 1/2, y = 0, z = 0. Some small residual peaks are often

observed in the Fourier difference maps, suggesting that a minor quantity of deuterium could possibly occupy additional positions. The most important results concern the behaviour of the D occupancy vs. temperature and pressure, which determine the thermodynamic and kinetic properties of the absorption/desorption processes of deuterium by the Pd-Ag alloy.

Table 1. Results of the Rietveld refinements of all diffraction patterns, reported in chronological order.

#	*P* bar	*T* °C	R_p %	R_B %	*a* Å	*a*(Al) Å	o.f.(D)	*B*(PdAg) Å^2	*B*(D) Å^2
1	≈ 0	196	8.02	8.26	3.9343(3)	4.062		0.9(3)	
2	1	241	8.02	5.00	3.95756(3)	4.068510(7)	0.084(11)	0.526(2)	1.5(7)
3	1	196	7.03	3.37	3.96740(3)	4.064507(7)	0.131(12)	0.526(2)	2.9(6)
4	1	79	6.47	2.45	3.98248(7)	4.05304	0.286(14)	3.5(4)	0.50(6)
5	1	79							
6	2	79							
7	2	79	6.78	4.49	4.01746(3)	4.05304	0.387(14)	0.67(5)	4.6(3)
		evacuation							
8	2	241	7.76	3.52	3.96912(3)	4.068752(8)	0.115(12)	0.519(2)	1.7(6)
9	2	196	9.99	4.63	3.99033(3)	4.064427(9)	0.227(18)	0.60(7)	4.6(6)
10	4	196	7.94	5.83	4.00488(2)	4.064485(7)	0.293(15)	0.74(5)	5.4(4)
		evacuation							
11	1	196	6.82	2.80	3.96979(3)	4.064398(7)	0.142(12)	0.522(2)	3.0(6)
12	1	79							
13	1	79	6.86	4.58	4.01476(3)	4.05304(6)	0.384(15)	0.52(5)	4.8(3)

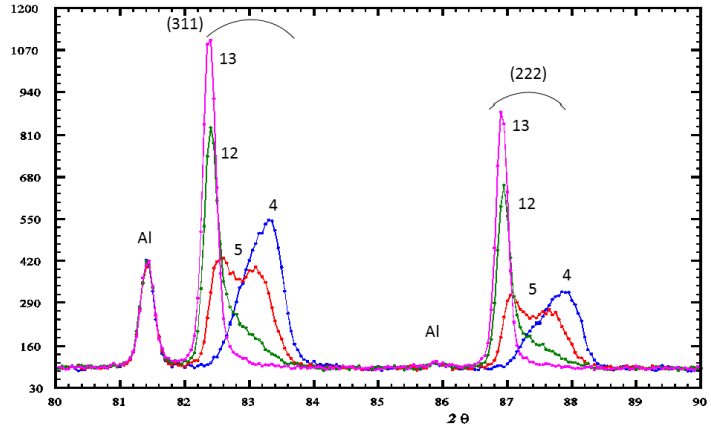

Fig. 2. Bragg peaks (311) and (222) of the four patterns n. 4, 5, 12, and 13 (cf. Table 1) collected at 79 °C and 1 bar at different times and with different pressure histories.

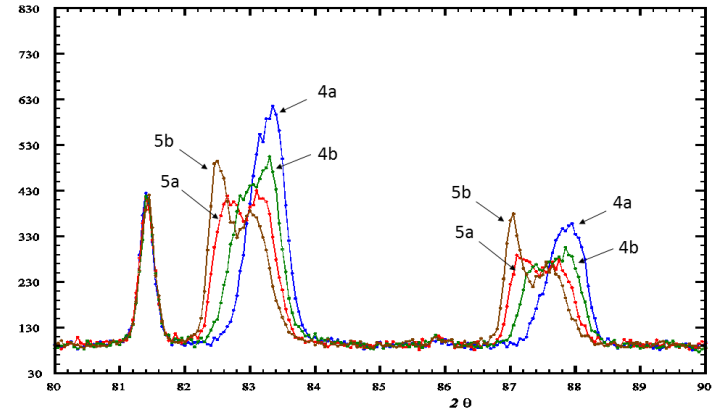

Fig. 3. As in Fig. 2, but runs n. 4 and 5 have been each split into the first time half (a) and second time half (b) of collected data. Runs n. 12 and 13 are not shown for clarity.

Refinement results are not reported in Table 1 for cases where the sample turned out to contain two different phases in variable amounts. This applies in particular to measurements at 79 °C and 1 bar (n. 4, 5, 12, 13). Two of them were performed consecutively during the first cooling cycle at 1 bar (n. 4 and 5), and two others consecutively after the thermal cycles at 2 and 4 bar (n. 12 and 13). On comparing the four patterns (Fig. 2), it appears that true equilibrium was attained only in the last measurement n. 13, after the pre-treatment at 4 bar and a sufficient elapsed time. On looking at the intermediate pattern n. 5, a two-phase state of the sample is inferred from the clear splitting of Bragg peaks. The two phases seem to be both FCC with different lattice parameters and correspondingly different amounts of absorbed deuterium: cf. the end cases of patterns n. 4 (a = 3.9825 Å, o.f.(D)= 0.286) and n. 13 (a = 4.0148 Å, o.f.(D) = 0.384). From the splitting of peaks observed in pattern n. 5, the a values of the two coexisting phases are estimated to be 3.988 and 4.008 Å. However, there are clear indications that the transformation between the two phases was in progress during the time of each data collection (2.7 h). Each pattern is obtained by merging the neutron counts from 10 separate angular scans (16 min each), which are collected consecutively and are stored in corresponding data files. Thus, on merging the first 5 data sets one obtains an approximate pattern for the first 80 minutes (pattern (a)), and on merging the last 5 data files for the last 80 min (pattern (b)). This was done for measurements n. 4 and 5, and the results are shown in Fig. 3: they thus correspond to four consecutive time steps of 80 min each. We can conclude that the transformation between the two phases was in progress during the 5.4 hours of the two measurements, and still not completed at the end. Only after the thermal treatments at 2 and 4 bar the equilibrium state of the expanded phase was reached (patterns n. 12 and 13). Yet it can be remarked that peaks in pattern n. 12 still show significant tails at their high angle sides (Fig. 2). This suggests that absorption is enhanced after several cycles of absorption/desorption above 2 bar.

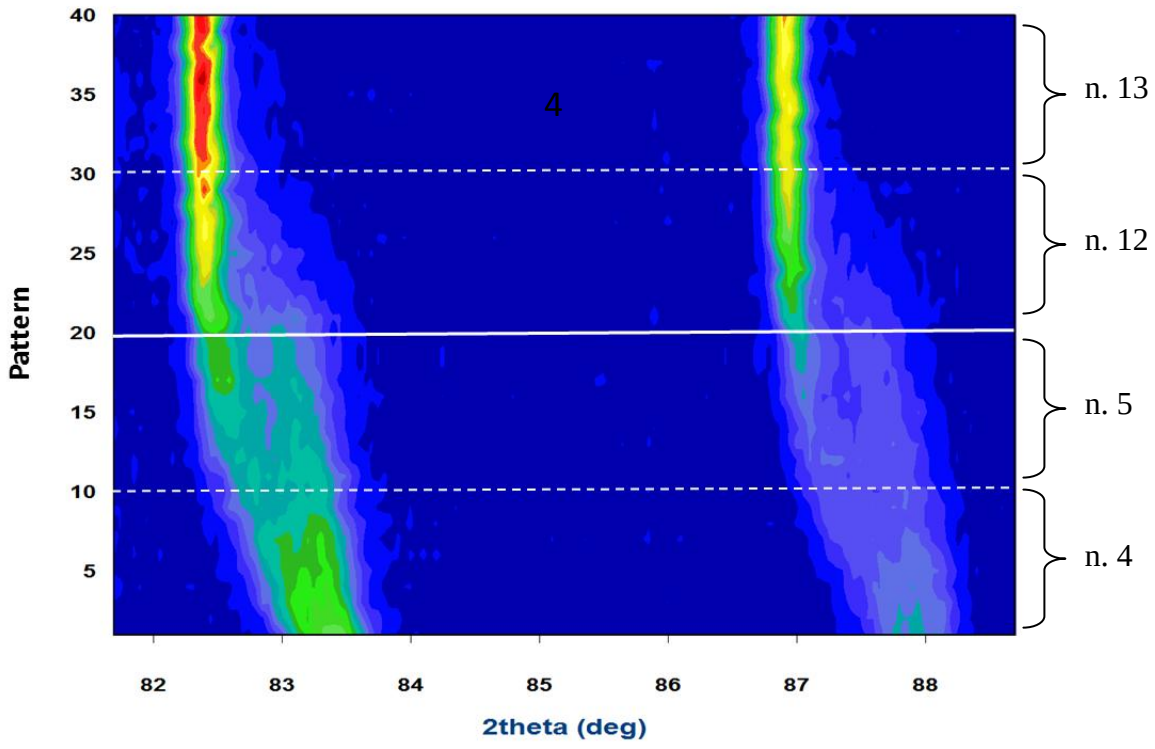

Fig. 4. Plot of the (311) and (222) peaks of $Pd_{0.77}Ag_{0.23}D_x$ from the 40 single patterns contributing to the merged patterns n. 4 (patterns 1-10), n. 5 (patterns 11-20), n. 12 (patterns 21-30), and n. 13 (patterns 31-40).

In Fig. 4 the intensities of all individual patterns contributing to runs n. 4, 5, 12, and 13 are represented without any merging.

Further work on the data analysis is in progress, particularly for results obtained at high pressure.