Experimental report

03/02/2016

Proposal:	**5-25-241**	**Council:**	4/2014
Title:	Neutron Diffraction measurements on Deuterated Pd/Ag alloy		
Research area:	Materials		

This proposal is a new proposal

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Samples: Pd-Ag with D2

Instrument	Requested days	Allocated days	From	To
D1B	3	2	14/10/2015	16/10/2015

Abstract:

Hydrogen selective based palladium membranes are important for technological processes such as separation and purification. In general, a Pd-membrane when hydrogenated becomes brittle after certain cycles of α  β hydride transformation due to the accompanied lattice expansion. In order to avoid the embrittlement, alloying of Pd with Ag is generally made. Differently, in Pd-Ag alloys, the lattice has already been expanded by the silver atoms, and the Pd-Ag lattice is less influenced by hydrogen uploading and then less brittle than the pure Pd lattice. We propose to analyze the deuterium filled Pd0.79-Ag0.21 alloy through neutron diffraction using the D1B (High resolution neutron two-axis powder diffractometer) beam line at ILL at constant pressure (100 kPa) and different temperatures, in the range T=100-160°C. This is the temperature region in which the electric resistivity of the alloy passes through the minimum and then it is the region in which it is likely to expect the interstitial tetrahedral sites of the FCC lattice should start to be filled up with deuterium.

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‘Neutron Diffraction measurements on Deuterated Pd/Ag alloy’

Experimental details

Neutron diffraction measurements by D1B were carried out in the 1 -128° 2θ range at λ= 1.2871 Å on a 0.05 mm thick foil of $Pd_{0.77}Ag_{0.23}$ alloy. The sample holder was a 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.

The metal foil was rolled up inside the holder, and a set of diffraction patterns were collected at different temperatures and D_2 pressures; in most cases the measurement time was 1 h. A critical experimental aspect was the T control. Owing to their different positions with respect to the heating element and to the sample, the two thermocouples indicated higher and lower temperatures, respectively, with respect to that expected on the sample itself, with T_1-T_2 ranging from 9 °C at 200 °C to 5 °C at 80 °C. The average $(T_1+T_2)/2$ was thus assumed as reasonable estimate of the sample temperature.

Four series of runs were performed, for a total of 24 collected patterns, with the following sequence: cooling at 1 bar, cooling at 2 bar, cooling at 4 bar, heating at 1 bar. In the cooling cycles the T_1 values were set at 200, 160, 140, 120, 100, 80 °C, and in the heating one at the same values in the reversed order. Between subsequent cooling cycles the sample holder was evacuated, refilled with deuterium at the appropriate pressure, and heated to 200 °C. Between subsequent runs in each cycle the temperature was changed, and then a waiting time of 0.5 h was allowed to stabilize the sample before data collection.

Rietveld refinements

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 profile fitting). For Al, only the unit-cell constant was refined in each pattern, keeping fixed the other Al parameters from the calibration results. As for $Pd_{0.77}Ag_{0.23}$, the unit-cell edge, the occupation factor of D (located on the Fm-3m 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.

Table 1. Results of the Rietveld refinements at p = 1 bar(D_2).

T_{sample} (°C)	R_p (%)	wR_p (%)	R_B(PdAg) (%)	a(PdAg) (Å)	a(Al) (Å)	o.f.(D)	B(PdAg) (Å^2)	B(D) (Å^2)
196	8.11	11.6	5.47	3.95720(9)	4.06192(6)	0.087(9)	1.10(4)	2.9(7)
159	7.28	10.4	4.58	3.96685(8)	4.05965(5)	0.118(8)	0.98(4)	3.4(5)
137	6.44	9.63	6.22	3.97716(9)	4.05663(5)	0.162(9)	1.10(4)	4.0(4)
117	6.38	9.34	5.80	3.98668(9)	4.05497(5)	0.207(9)	0.93(4)	3.9(3)
98	6.48	9.97	4.54	3.9934(1)	4.05335(5)	0.242(9)	0.90(4)	4.0(3)
78	6.72	10.2	4.69	3.9958(1)	4.05151(6)	0.263(10)	0.87(4)	4.0(3)

A major problem with the Rietveld refinement of the deuterated alloy was the observed overlap of some of its Bragg peaks with some from the aluminium cell; this was the case particularly in the low T range (below 140 °C), because the thermal expansion coefficient of the Pd/Ag alloy turns out to be much larger than that of aluminium, so that the overlap increases on cooling (cf. Figs. 1 and 2). A better instrumental resolution would be needed to cope with this issue.

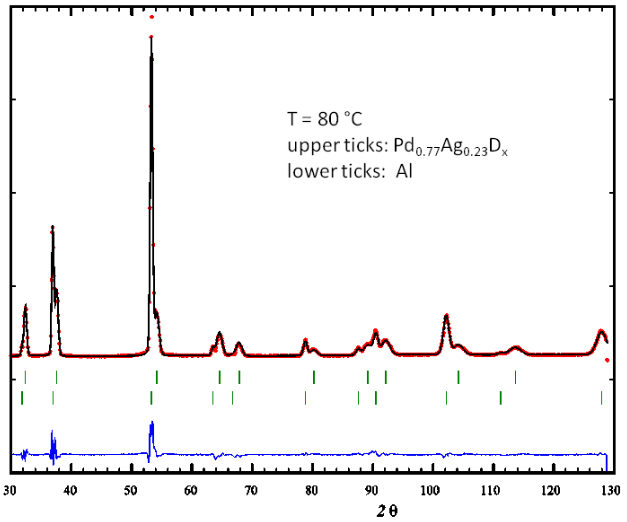

Fig. 1. Diffraction pattern recorded at 80 °C.

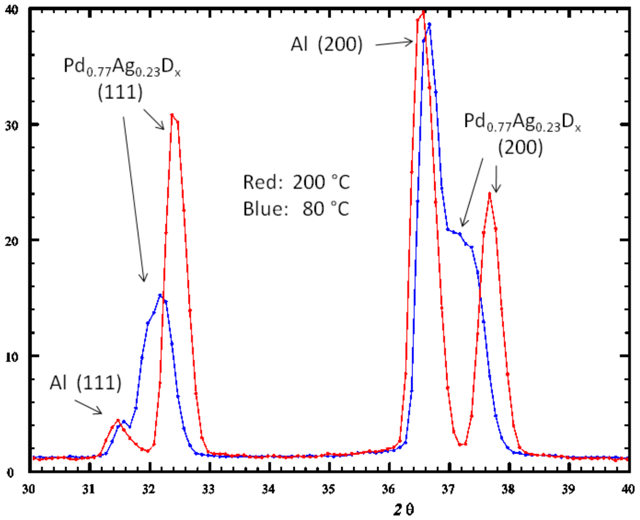

Fig. 2. Diffraction patterns recorded at 80 and 200 °C (2θ = 30-40° range).

Location of D atoms

Fourier difference maps calculated before inserting D atoms showed only a strong peak at ½,0,0 (octahedral site). After including the D atom in that position in the refinement, two small residual peaks appeared at 0.26,0,0 and at ¼,¼,¼ , which however could not be refined as additional D atoms. Thus, it cannot be excluded that a minor quantity of deuterium is present also in the tetrahedral site and in disordered locations around the octahedral site. A better quality of data at improved resolution is necessary to solve this problem.

Thermal and pressure behaviour

The refined D occupation factor in the octahedral site (x value in the $Pd_{0.772}Ag_{0.228}D_x$ formula) is plotted vs. T for the three cooling cycles at different pressures in Fig. 3.

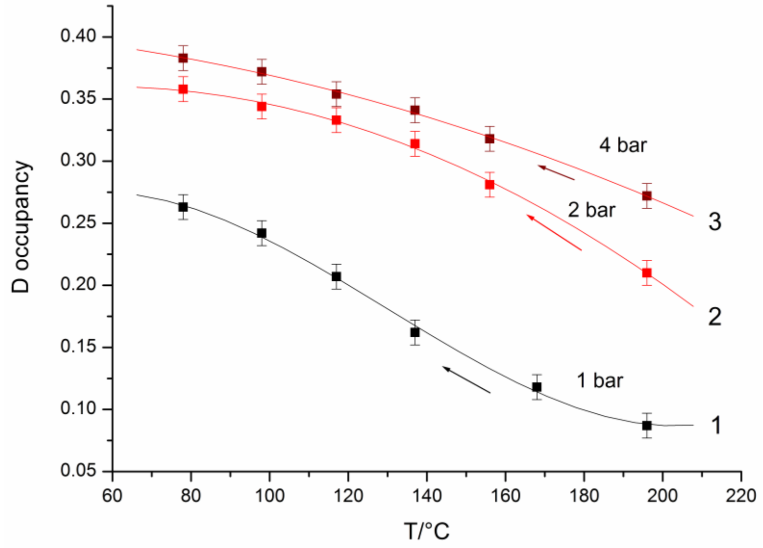

Fig. 3

Results coming from the last heating cycle of runs have not been reported, because the large values of D content obtained suggest that residual deuterium from the previous cycle may have not been removed completely.

The amount of absorbed deuterium at room pressure inferred by Fig. 3 is somehow lower than that reported in the literature for hydrogen, at corresponding temperatures, on the basis of thermodynamic measurements. This discrepancy may be due the D/H isotopic effect, but it could also indicate that a minor quantity of D located on non-octahedral sites was not accounted for in the structure refinement, because of insufficient quality of data (cf. the issue of peak overlap with Al from the cell, and the limited instrumental resolution).

Data obtained at 1 bar can be fitted by a cubic curve, showing an inflexion point at about 150 °C. This behaviour agrees nicely with results previously published by members of this research group on thermodynamic and electric measurements of the effects of H_2 absorption by the PdAg alloy. On the other hand, no inflexion point appears in the fit of data at higher pressures. However, on extrapolating the fitting curves for such cases we can reasonably suppose that the inflexion point would appear at higher temperature. Further measurements extending the range of temperatures and pressures are needed to settle this open point.

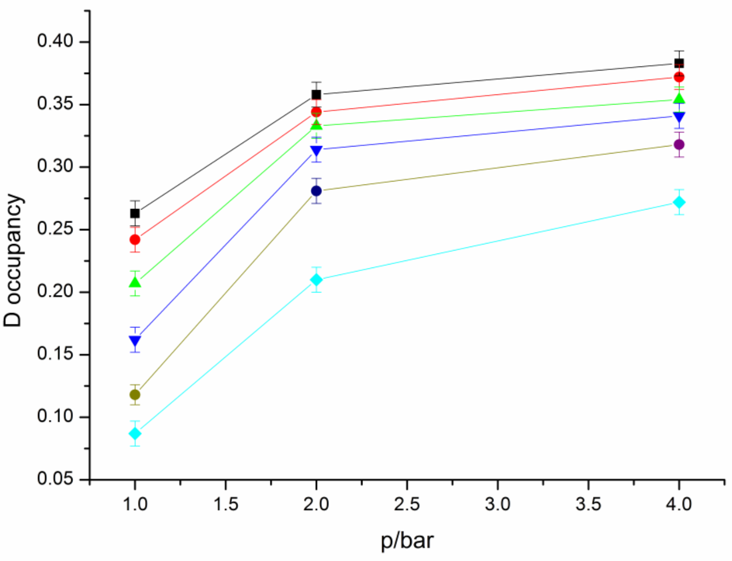

Fig. 4. Deuterium occupancy (x value in the $Pd_{0.772}Ag_{0.228}D_x$ formula) plotted vs. D_2 pressure at different temperatures (80, 100, 120, 140, 160, 200 °C).

The behaviour of D occupancy in the octahedral site vs. pressure (Fig. 4) shows an appreciable negative deviation from the expected square-root-like dependence: a sort of saturation effect is observed, particularly in the 2 to 4 bar range at lower temperature. This is another critical point of the results which requires further experiments at better resolution, in order to test the possible presence of deuterium in non-octahedral sites accounting for the low quantity of D observed.

(uploaded by Michele Catti on 3/2/2016)