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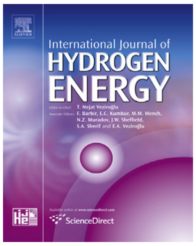

Neutron diffraction study of the $Pd_{0.772}Ag_{0.228}D_{\nu}$ membrane for hydrogen separation

M. Catti [a,*], O. Fabelo [b], A. Filabozzi [c], A. Pietropaolo [d], S. Tosti [d], A. Pozio [d], A. Santucci [d]

[a] Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, via Cozzi 55, 20125, Milano, Italy
[b] Institut Laue-Langevin, 71 avenue des Martyrs, 38000, Grenoble, France
[c] Dipartimento di Fisica, Università di Roma Tor Vergata, via della Ricerca Scientifica 1, 00133, Roma, Italy
[d] ENEA, Dipartimento Fusione e Tecnologie per la Sicurezza Nucleare, via Fermi 45, 00044, Frascati, Italy

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ABSTRACT

Experiments of deuterium absorption/desorption were performed on a foil of $Pd_{77}Ag_{23}$ (wt %) alloy in the 78–196 °C temperature and 1–4 bar pressure ranges under the neutron beam at ILL (Grenoble). Powder diffraction patterns were collected on the D1B diffractometer ($\lambda = 1.2871$ Å) on the $Pd_{0.772}Ag_{0.228}D_{\nu}$ deuterated alloy, and the face-centred-cubic structure was Rietveld-refined locating the D atom in the octahedral site with a variable occupancy ν (=D/M ratio). The results of $\nu(T)$ curves at different $p(D_2)$ pressures are discussed in comparison with literature data on H and D absorption into Pd–Ag alloys from thermodynamic measurements. A negative deviation from predictions of Sieverts' law is shown by the dependence of D occupancy on pressure. This effect relates the behaviour of the activity coefficient γ_D to D–D and D–M interactions in the solid solution phase.

Introduction

Exploiting hydrogen as energy carrier for renewable energy sources is expected to reduce the emissions of greenhouse gases in the atmosphere [1–3]. However, a hydrogen-based economy requires that a well-proven technological platform for the safe and reliable hydrogen production, separation, storage and transportation is developed [4]. In particular, hydrogen production and separation could take advantage of the membrane processes that arose an increasing interest in recent years, because of their reduced energy consumption and continuous operation mode [5–9]. Further, these processes can be easily scaled up and integrated with other separation technologies.

Thanks to the unique property of hydrogen to pass through dense metal walls, metal membranes were introduced for separating hydrogen from gas mixtures selectively. The Pd–Ag alloy with silver content around 25 wt.% exhibits the best hydrogen permeability and mechanical strength, with heavily reduced embrittlement effects [10]. Therefore, Pd–Ag alloys with this composition are now commercially available for the manufacturing of membrane devices used for both hydrogen separation (permeators/diffusers) and hydrogen production (membrane reactors) [11,12]. The further optimization of the Pd-membrane devices requires a deep understanding of the chemical–physical properties of the hydrogenated Pd-alloys in the range of the operating conditions typical of the membrane processes (temperature up to 400–450 °C and pressure up to 10–20 bar).

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* Corresponding author.
E-mail address: michele.catti@mater.unimib.it (M. Catti).

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Recently, hydrogen permeators were ohmically heated by applying an electric current directly through thin-walled Pd–Ag tubes [13]. In order to properly design these membrane modules, the strain and electrical resistance of hydrogenated Pd–Ag tubes were measured from 100 to 400 °C [14], while below 100 °C some anomalies of the electrical resistivity were observed and not reported in that study. In subsequent experiments, the electric properties of a thin Pd–Ag strip were studied in detail, finding a S-shaped curve of the resistivity vs. both temperature and hydrogen pressure [15]. This peculiar behaviour was tentatively explained in terms of an interaction of the conduction electrons with H atoms in the Pd–Ag structure. Although structural properties of pure hydrogenated Pd were studied extensively [16–18], those of Pd–Ag alloys require further investigations, in particular as a function of hydrogen uploading.

A study was thus undertaken with the purpose of determining (i) the location of D/H atoms absorbed inside the FCC structure of the $Pd_{77}Ag_{23}$ alloy, (ii) the amount of D/H dissolved in the alloy structure at different temperature and pressure values, and (iii) the change of volume accompanying the gas uptake in the solid solution. In order to have direct access to atomic-scale structural information diffraction methods are the best choice. However, H atoms scatter X-rays very weakly, while with neutrons they produce a huge incoherent background limiting severely the accuracy of measurement of diffraction intensity. The last case does not apply if deuterium is used, as this behaves as a strong coherent scattering centre for neutrons. For this reason, we chose deuterium rather than hydrogen gas for in-situ absorption studies by the $Pd_{77}Ag_{23}$ alloy under thermal neutron beam irradiation. Indeed, the technique of D/H isotopic substitution coupled with neutron diffraction proved quite successful for investigating the structural properties of several hydrogen storage materials [19–21]. A convenient range of temperature and $p(D_2)$ pressure conditions was explored in the course of these absorption experiments.

Experimental

The sample used was a 0.05 mm thick (70 × 135 mm) foil of $Pd_{77}Ag_{23}$ (wt%) alloy purchased from Goodfellow Cambridge Ltd. Neutron diffraction patterns were collected on the D1B medium resolution-high-flux diffractometer at the Institut Laue-Langevin (Grenoble, France), in the 1–128° 2θ range with $\lambda = 1.2871$ Å; in most cases the measurement time was 1 h. The metal foil was rolled up inside an Al can provided with a heating system and connected to a gas manifold, which allowed the holder to be evacuated and filled with D_2 gas at variable pressure. A preliminary diffraction pattern was collected on the foil within a standard vanadium holder, and the Rietveld analysis showed that preferential orientation had negligible effects on the sample. A pattern was recorded also on the empty Al pressure cell, and it was analysed by profile matching method with constant relative intensities. This fit was later included in all main refinements of the deuterated alloy as a second phase, where the only free parameters were the scale factor and the cell parameter. For pure $Pd_{77}Ag_{23}$ the cubic lattice constant of 3.9274(1) Å was obtained at room temperature, slightly lower than the X-ray value of 3.929(1) Å previously reported [22].

A critical experimental aspect was the temperature control. Due to the heavy mass of the pressure cell, the regulation thermocouple (close to the heating element within the cryostat) measured a slightly higher value (T_1), and the thermocouple located in the sample stick a slightly lower value (T_2) with respect to that expected on the sample. The average $(T_1 + T_2)/2$ was thus assumed as reasonable estimate of the sample temperature.

Three cooling cycles were performed at different constant pressures, namely $p(D_2) = 1$, 2, and 4 bar. Each one consisted of six data collections at $T = 196$, 157, 137, 117, 98, 78 °C, for a total of 18 diffraction patterns. After the first and second cycles the sample holder was reheated to 196 °C, the pressure increased, and the next cooling cycle started. At the end of the 4 bar run the holder was pump-evacuated at 78 °C, D_2 was pumped in again to 1 bar, and a final heating cycle was carried out at that pressure, collecting data at $T = 78$, 98, 117, 137, 157, 196 °C.

Between each temperature change at constant pressure, a waiting time of 0.5 h was applied to thermalize the sample before starting data collection.

Results and discussion

Analysis of data and structure refinements

All collected patterns were analysed by the FullProf suite [23], including two phases in the profile refinement: the face-centred-cubic (FCC) $Pd_{0.772}Ag_{0.228}D_v$ deuterated alloy (Rietveld refinement), and FCC aluminium (profile matching with constant relative intensities) to include the sample environment reflections. The background was linearly interpolated by a set of fixed points. Bragg peaks were modelled by a pseudo-Voigt function (linear combination of Gaussian and Lorentzian components, with σ and γ half-widths, respectively). The σ and γ parameters vary with θ as $\sigma = (U \tan^2\theta + V \tan\theta + W + P/\cos^2\theta)^{1/2}$ and $\gamma = X \tan\theta + Y/\cos\theta$; the U, V and W coefficients are mainly related to instrumental resolution, P and Y are the Scherrer coefficients for Gaussian and Lorentzian particle size broadening, respectively, and X is related to particle strain broadening. The mixing coefficient and the full width of the pseudo-Voigt function depend on σ and γ according to equations given in the literature [24]. For Al, only the unit-cell constant and the scale factor were refined in each pattern, keeping fixed the other Al parameters from the calibration results of the empty cell. For the main $Fm\bar{3}m$ phase ($Pd_{0.772}Ag_{0.228}D_v$) the scale factor, the unit-cell edge, the displacement factors of $Pd_{0.772}Ag_{0.228}$ and of D, and the U, V, W, Y profile parameters were always refined. Slight changes of U, V and W indicated a weak dependence of these parameters on experimental conditions of the sample, in addition to instrumental resolution.

A Fourier difference map was calculated before inserting D atoms, and it showed only a strong peak at $x = ½$, $y = 0$, $z = 0$ (octahedral site). After including the D atom in that position in the refinement, with a variable occupation factor and displacement factor, a subsequent Fourier difference map showed two weak residual peaks at 0.26,0,0 and ¼,¼,¼