ESRF	**Experiment title:** **Microstructural characterisation of Pd-based thin-film membranes for hydrogen separation**	**Experiment number**: 01-01-785
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Names and affiliations of applicants (* indicates experimentalists):

John C. Walmsley, SINTEF Materials Technology, Applied Physics, Hogskoleringen 5, N-7465 Trondheim, Norway

Mathiesen, Ragnvald H.*, Dept. of Physics, NTNU, N-7491 Trondheim, Norway.

Wakshum Mekonnen T.*, Dept. of Physics, NTNU, N-7491 Trondheim, Norway.

Report:

Microstructures of free-standing, thin films (1.5 – 10μm thick) of Pd – based alloys utilized for hydrogen separation system have been studied by high-resolution XRD at ambient condition. The samples were pure Pd, Pd 23/ wt.% Ag and Pd 23/ wt.% AgY(3%).

The objective of the study was to investigate the microstructure of the Pd-based films/membranes, in general, and changes that might occur as a result of different experimental conditions during hydrogen permeation experiments. Results extracted from the XRD investigations, such as grain sizes, residual strains and lattice parameters, as well as their through-film thickness gradients would then be combined with information obtained from other experiments (permeation test, HRTEM, SEM, STEM/EDS) to arrive at a better understanding of factors that affect hydrogen transport through Pd-based membranes.

The samples were produced by magnetron sputtering technique on a Si wafer and then removed from the substrate, as free-standing, to use for testing and characterization. The samples studied at SNBL can be divided in to two categories: membranes tested for hydrogen permeation (at 300 ºC) and as-grown. Prior to permeation experiments the samples in the former category were annealed at 300, 400 or 450ºC in inert atmosphere or annealed at 300ºC in air for thermal activation purpose. The as-grown samples are simply pulled-off films that were not tested or subjected to post deposition heat treatment conditions. Since the grain structures at the two film surfaces differ, diffractograms were collected from both sides for each sample employing a near gracing incidence diffraction (GID) geometry. All together, 24 diffractograms were collected from a total of 6 tested and 6 as-grown films.

A piece of each film was fixed on a flat and smooth Pyrex glass plate by thin adhesive tape, and mounted onto the goniometer. Referring to a Cartesian laboratory frame ($\mathbf{x} \parallel \mathbf{k_0}$, $\mathbf{z} \parallel -\mathbf{g}$), the sample was mounted with its surface normal || **y**, and then aligned into a quasi GID by a rotation 1-2º about **z**. The films are associated with a rather prominent growth texture with <111> preferentially aligned in the growth direction. Therefore a texture mapping goniometer stage was employed to enable search for a position where all reflections in the 2θ-range 19-42º would appear with a reasonable signal-to-background. A suitable orientation was found at ~ 15º (rot. about **x**). Furtheremore, to scramble the effects of surface topography the sample was oscillated by ~ 0.5º about the surface normal during data collection. The incident beam was monochromatized to 15.5 keV, and a step length Δ2θ = 0.003º with 1 s counting per step was used consistently throughout the experiment.

Fitting and refinement of the data has been carried out in GSAS (A. C. Larson & R. B. Von Dreele, Report LAUR 86-784(2004)), employing standard models to separate the size and strain dependant parts of the peak profile broadening, arriving at a Pseudo-Voigt where the Gaussian and Lorenzian parts contribute to strain and size effects, respectively. In order to understand changes that might have occurred due to elevated temperature and pressure treatments, the microstructures of tested samples were compared with similar properties of as-grown for the same thickness and composition. As expected, the tested samples show increased grain size and reduced micro-strain. An example from the analysis is given in Figure 1 showing diffraction peaks of as-grown and tested 2.6 µm thick films of Pd23/wt%Ag, both scanned with the substrate-interface facing upwards. The tested sample has been exposed to a temperature of 400ºC and above for more than 100 days. As the peak broadening in Figure 1 shows, the tested sample has experienced both substantial grain growth and strain relief, with the grains grown to about twice their original size, and the average microstrain reduced by about 80% due to the annealing. The grain size of the samples of the same material scanned from the growth surface was nearly unchanged by the temperature processing. Absence of satellite peaks on the other hand confirms the alloy is stable at elevated temperature of operation. In general, grain size is temperature dependent for the samples annealed in inert atmosphere. A substantial grain growth was observed for temperature at 450 C and above.

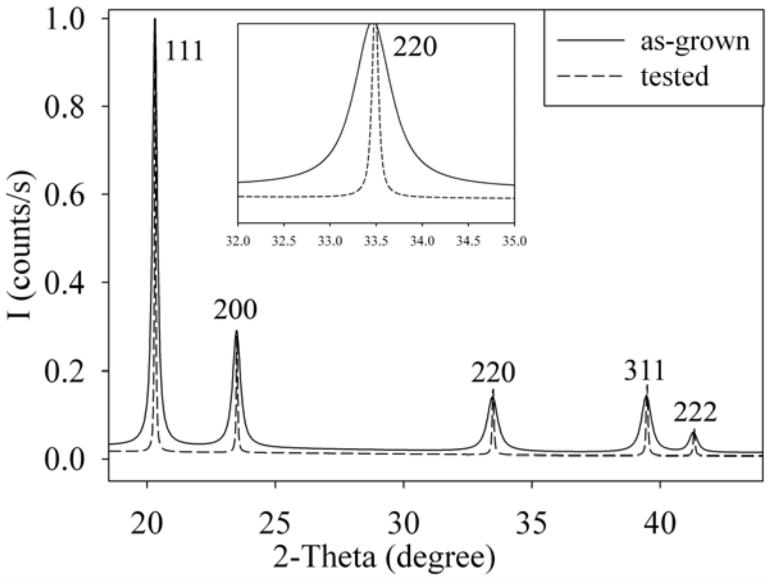

Figure 1: XRD diffractograms of as-grown and tested samples scanned from substrate-interface surfaces. The dashed-line peaks are for the tested membrane The inset shows magnified 220 peaks of both samples. Both samples are a binary alloy of Pd23/wt%Ag.

The whole data processing is still in progress, yet the analysis for some of the films is completed and the results have been already applied to improve our hydrogen transport models. A paper focusing on microstructure investigations of films tested for hydrogen permeation in air/inert atmosphere is in preparation for submission. We have also planned to publish at least two more papers using results from 01-01-785, together with results from bulk and surface studies by electron microscope to address permeation properties under long-term stability tests. Furthermore, details of as-grown microstructure (how lattice constants, grain sizes, micro-strains, dislocation densities, vary with film compositions and thicknesses) will be reported. The investigations are believed to provide useful inputs for the on-going efforts for optimizing functional Pd-based hydrogen permeation membranes.