

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.


Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Hydrogen loading of thin films	Experiment number: SI-2266
Beamline: B20	Date of experiment: from: 02/03/2011 to: 08/03/2011	Date of report: <i>Receivsd at ESRF:</i>
Shifts: 21	Local contact(s): Dr. Carsten Baehtz	
Names and affiliations of applicants (* indicates experimentalists): Helmut-Takahiro Uchida ^{*1} , Stefan Wagner ^{*1} , Astrid Pundt ¹ Marian Vlcek ^{*2} , Frantrisek Lukac ^{*2} , Jakub Cizek ² ¹ Institute of Materials Physics, University of Göttingen, 37077 Göttingen, Germany ² Faculty of Mathematics and Physics, Charles University, 18000 Praha 8, Czech Republic		

Report:

The change of a systems dimension is known to influence the physical properties. This effect will be remarkable when the system dimension is reduced to the order of nano-size, yielding different phase boundaries in phase diagrams and different mechanisms of phase precipitation. [1-3]

To study the impact of both microstructure and mechanical stress contributions on the thermodynamics of nano-sized systems, series of electrochemical hydrogen loading experiments have been carried out at BM 20 for different metal-hydrogen thin film systems (Pd, Mg) with different initial film thicknesses in the range from 16 to 1400 nm and different loading conditions.

For 16 nm epitaxial Pd thin films it was shown that thickness fringes reappear after film loading up to concentrations of $c_H = 0.90$ H/Pd, revealing that phase boundaries between α - and β -phase stay coherent throughout reversible phase transformations [4]. However, even for these very thin films the α -phase out-of-plane lattice parameter was shifted systematically to values smaller than the lattice parameter of the pristine film, showing that misfit dislocations form between the film and the substrate during H-loading, see **Fig.1**.

As the second part, nanocrystalline 1400 nm of Mg-films have been investigated. Mg has been identified as one of the promising candidates owing to the high hydrogen content (7.6wt%) of its hydride. However, Baldi *et al.* [5] reported that it is not possible to completely hydride Mg thin films with more than 100 nm thickness because of the formation of a surface hydride blocking layer. Recently, we reported that hydride formation is possible for Mg-film thickness up to 188 nm by electrochemical loading technique, and that the thickness of the hydride layer can be tuned by proper loading condidtions, even at room temperature [6]. In this measurements, we focused on the influence of loading current density on the evolution of inner stress of nanocrystalline Mg-films, by monitoring bragg peak during electrochemical hydrogen loading. In-plane stress states were calculated for each peak position that reveal out-of-plane lattice distorsion [7], applying elastic properties of the material and stress-free bulk lattice parameters as reference.[8] Phase transition kinetics at several hydrogen concentrations was also evaluated, by monitoring the relative peak area change of Mg (0002) reflection at each hydrogen concentration, as it is consumed by nucleation of thehydride phase.

Mg films were deposited on Si (100) substrates at room temperature by means of Ar-sputtering method. 20 nm of Pd layers were also deposited before and after Mg deposition, to prevent oxidation and corrosion due to a contact with the electrolyte. A Mg (0002) texture was observed for the prsitine samples. An investigation of the reflex positions of the coherent MgH_2 -(110) peak was complementarily done in this measurement. Two different hydrogen loading conditions of the maximum current density (i [A/cm²]) were adopted, $i < 4 \cdot 10^{-6}$ for Sample 1 and $i < 2 \cdot 10^{-5}$ for Sample 2, respectively. Hydrogenation kinetics was

evaluated from the relative peak area change of Mg (0002) at each hydrogen concentration. Plotting the growth of hydride layer thickness as a function of squareroot of time yields the diffusion constant of hydrogen. This evaluation is possible as far as the bending of the substrate is negligible. Upon hydrogenation, a crystallographic orientation matching of Mg-(0002)/MgH₂-(110) is known [6].

Fig.2 shows the result of the change of the Mg (0002) peak at each hydrogen concentration in equilibrium states. Both samples revealed increasing compressive stress change to the initial state up to $\Delta\sigma = -0.4$ GPa (Sample 1) and $\Delta\sigma = -0.25$ GPa (Sample 2) in the hydrogenation processes, being charged up to $c_H = 5 \cdot 10^{-3}$ H/M (Sample 1) and $c_H = 7 \cdot 10^{-3}$ H/M (Sample 2). Here, the tensile direction is defined as positive direction of the σ . Comparing at $c_H = 5 \cdot 10^{-3}$ H/M, the slowly loaded Sample 1 achieved $\Delta\sigma = -0.4$ GPa, which is larger than that of Sample 2 ($\Delta\sigma = -0.06$). Both sample revealed a decrease of the in-plane compressive stress for further hydrogenation. This is attributed to a detachment of the films, optically observed after the loading. Obtained diffusion constants decrease logarithmically from the order of $10^{-11} \text{ m}^2\text{s}^{-1}$ ($c_H < 10^{-3}$) to $10^{-16} \text{ m}^2\text{s}^{-1}$ ($10^{-2} < c_H < 10^{-1}$) as the hydrogen concentration increases. However, these values are more than 3 orders larger than the diffusion constants of hydrogen in the bulk pure Mg at room temperature ($10^{-20} \text{ m}^2\text{s}^{-1}$), reported by Spatz *et.al.* [9] This indicates that grain boundaries are an important pathway for hydrogenation of nanocrystalline Mg films, especially at higher hydrogen concentrations.

Fig.3 shows the Bragg-Peak of the β -MgH₂ (110), in the concentration range of $c_H = 5 \cdot 10^{-5}$ to $c_H = 4 \cdot 10^{-4}$ for sample 1. Crystallographic orientation matching for the thin films results in strong intensity loss. The maximum intensity and best S/N ratio peaks of the hydride peak for both samples were observed at a tilting degree range of $\varphi = 2.0 - 3.5$. Deviated distributions of coherent reflex positions could possibly apply for the hydride sub-lattice.

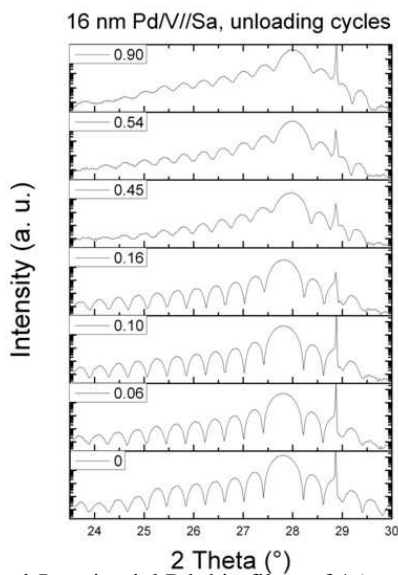


Fig.1 In epitaxial Pd thin films of 16 nm thickness thickness fringes re-appear reversibly after loading the films up to $c_H = 0.90$ H/Pd..

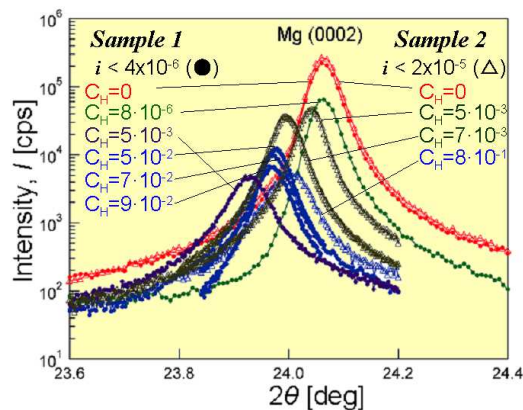


Fig.2 XRD peaks of Mg (0002) of Sample 1 and Sample 2 at each hydrogen concentrations ($c_H = \text{H/Mg}$), described in the left side and the right side, respectively.

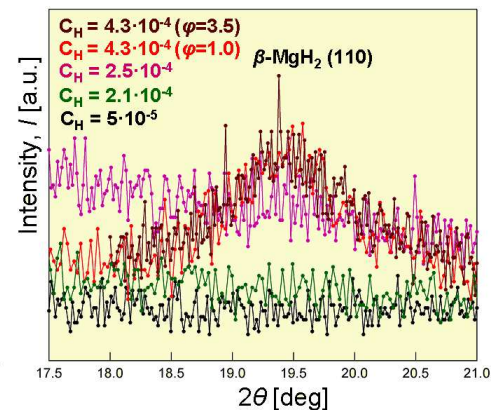


Fig.3 The MgH₂ (110) change for the Sample 1 at several hydrogen concentration degrees. Psi-angle is tilted for the curve of $c_H = 4.3 \cdot 10^{-4}$, to the maximum intensity.

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