In nano-sized systems like metal hydrogen thin films undergoing structural phase transitions, when the system size is reduced below a critical dimension, the thermodynamics of the phase transitions is expected to change: For large systems microstructural stress can relax by the incorporation of misfit dislocations, irreversibly forming incoherent interphase boundaries. For systems below a critical size, stress relaxation is expected to be energetically not favorable [1]. This yields a new kind of coherent thermodynamics which is ruled by the interfacial stress, not taken into account in conventional Gibbs thermodynamics [2]. Hence, such systems might stay coherent throughout the complete phase transition [1-4] and possess different kinetics.

Applying Nb-H and Pd-H as a model system, we are investigating the influence of critical film thickness on the thermodynamics and kinetics of phase transformation by applying in-situ hydrogen loading during XRD measurements on Beamline P08. Samples were charged and discharged electrochemically and from the gas phase. Accompanying changes of the out-of-plane lattice parameters and the generation of hydride phases were monitored on site by means of Bragg-Geometry. According to our recent studies we expect a change in thermodynamics at the critical dimension between 25 and 27 nm [3,4]. Therefore, Nb and Pd films with a thickness below and slightly above these values have been studied. We focus on Nb in this report.

In the first part of our experiments samples were in-situ loaded from hydrogen gas atmosphere with defined pressures between 1·10^-5 mbar and 800 mbar. In Fig. 1, the (110) diffraction pattern evolution of a 30 nm Nb-H film is shown in dependence on hydrogen pressure and exposure time at this pressure. As soon as hydride phase starts to grow, thickness fringes disappeared - reflecting on lattice deterioration during hydride precipitation and loss of coherency on the hydride/ surrounding α-matrix interface or between film and substrate. Precipitation of the hydride phase and appearance of second peak have been firstly observed after 36 min of sample exposure to 7.8·10^-2 mbar of hydrogen pressure. Our measurements performed with Nb thin film covered with 20 nm Pd capping layer demonstrated unexpected slow kinetics at low hydrogen pressure in a broad pressure range from 1·10^-6 mbar to 1·10^-2 mbar for all Nb samples. In accordance to this finding, a strongly increased phase transition pressure in comparison to the bulk was observed [5]. Thereby, a possible impact of the required Pd capping layer on the hydrogen absorption in thin Nb films needs to be separated from coherency stress contributions by varying the capping layer’s thickness. Coherency stress seems to affect the hydrogenation kinetics and phase transition pressure in thin Nb-H films and needs further investigation. The time scale for the complete transformation to the hydride phase at these conditions was found to vary between 40 and 120 min depending on the film thickness and applied hydrogen pressure. Details will be published elsewhere.
Unfortunately, the high speed option with the 2-D detector was not available in the Bragg-reflection measurements. Thereby, the spatial orientation of the crystal planes and crystal structure of precipitates change during sample hydrogenation require further investigation. Additionally, to find the correlation between the critical stress and coherency conservation in-homogeneous stress measurements are required and plan to be done by using IMP setup in near future.

In the second part of our experiments samples were loaded and unloaded electrochemically. The experiments showed that Nb samples wetted with electrolyte posses auto-catalytic transformation to the hydride phase under interaction with X-Ray beam. Thereby, after each loading step the electrolyte was removed from the film in order to perform XRD scans at fixed hydrogen concentration. In Fig. 2 the (110) diffraction pattern evolution of 20 nm Nb-H is shown as a function of hydrogen concentration. No peak splitting was found during hydride formation, conventionally appearing during phase separation for Me-H systems above the critical film thickness. Only one broad peak moving forward to the lower angle range has been observed, revealing the conservation of coherency at the hydride/α- matrix interface. This means that indeed the mechanism of hydride formation differs for thin and thick films. In comparison with the 30 nm and 40 nm films, thickness fringes disappeared only at hydrogen concentrations of about 0.33 H/M, well above the solubility limit c_α for the addressed thickness range. Conservation of thickness fringes reveals very smooth surface conditions and strong coherent match between the lattice planes of different phases, meaning the shift of critical concentration for the activation of the stress relaxation process for 20 nm Nb-H thin film system. However, at large hydrogen concentrations dislocations may form at the film-substrate-interface.

**Figure 1**: (110) XRD patterns for 30 nm Nb-H, incoherent phase transition regime; precipitation of second hydride related peak is visible. Volume fractions of α and β phase can be considered separately. Thickness fringes disappear as soon as hydride phase start to form.

**Figure 2**: (110) XRD patterns for 20 nm NbH, coherent phase transition regime; only one broad peak is visible. Thickness fringes disappear in the middle of the two phase region only; critical concentration for activation of stress relaxation processes is shifted.

**References:**