In-situ XRD measurement of nanocrystalline Magnesium films during hydrogen loading

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Magnesium hydride (MgH₂) has potential as a safe hydrogen storage material because of its high hydrogen capacity of 7.6 wt.%. However, its slow sorption rate prevents its practical use. This slow hydrogen sorption rate is caused by the MgH₂ itself that nucleates during hydrogen sorption and blocks additional hydrogen diffusion ("Blocking effect") [1]. Important roles of microstructure on hydrogenation properties are reported [2], and the influence of grain boundaries as a bypass on hydrogenation properties of magnesium films is recently discussed [3].

Magnesium films with the thickness between 500 nm and 2500 nm were prepared on Si(100) substrate by Ar-ion sputtering technique in an UHV system, at room temperature. The surface of films was capped by 20nm thick Pd layers to prevent oxidation.

The samples were investigated at room temperature in standard θ-2θ geometry (λ = 0.9995 Å) at beamline B2 at Hasylab (DESY) in-situ during hydrogen gas loading. The loading was performed in a specially designed loading cell with a capton window and automatic valves. The loading gas pressures were between 10⁻⁴ mbar and 200 mbar.

Fig.1 shows the change of XRD patterns of the α-Mg(0002) peak, during hydrogenation. Before hydride peak appears, the α-Mg(0002)-peak decreases rapidly. After hydride nucleation, the decrease of the α-Mg(0002) peak slowed down. The α-Mg(0002) peak typically remains after hydrogenation treatment of several hours. The peak of Pd (111) which comes from the surface layer was observed just in the beginning, and rapidly disappeared as hydrogenation started, due to the increasing surface roughness.

Since magnesium hydride has high electric resistivity, it is valid to apply in-situ four-point measurement to monitor the nucleation of MgH₂ phase. Fig.2 shows the relative change of resistivity (R/R₀) as a function of time of hydrogenation, which is measured in-situ by the four-point measurement technique. The hydrogen pressure condition was set as constant pressure (200mbar) at room temperature. Resistivity obviously strongly increases when the hydride nucleation is visible in the in-situ XRD measurement. The resistivity before and after hydrogenation treatment R/R₀ varies from a factor 2 to 220 due to the different thicknesses of the films. The resistivity change of the 2500 nm-magnesium film was continuously and almost constantly increased, still increasing after loading for 3 hours. This shows the reaction of 2500 nm-thick Mg film was not completed within 3 hours. On the other hand, magnesium films thinner than 750 nm showed constant values within the loading time of 3 hours. Nevertheless the α-Mg(0002) peak still remained.

Diffusion constants of hydrogen in magnesium are calculated from the change of volume fraction, which can be calculated from the Mg-peak area changes. Obtained values for the lower hydrogen concentration (loading time < 30 min.) and the values at longer hydrogenated states (t > 3 hours) are plotted and compared with extrapolated values from the reports of high-temperature measurements in Fig.3. Differences of more than 5 orders
of magnitude are visible in the obtained values between that of in the beginning and after long hydrogenated state.

Fig. 1: Change of α-Mg(0002) peak of 500 nm Mg on Si (001) during hydrogen loading with the constant pressure of 200 mbar.

Fig. 2: Relative change of resistivities of Mg films (Thickness of 500nm, 750nm and 2500nm) during hydrogenation under a constant pressure of 200 mbar, as a function of loading time.

Fig. 3: Obtained diffusion coefficient of hydrogen in magnesium, calculated from volume fraction change (decrease of Mg-peak area change) for the samples during hydrogen loading with the constant pressure of 200 mbar.

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References