Hydrogen sorption of Nb-catalysed, nanostructured Mg

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Mg is one of the most promising hydrogen storage materials with a capacity of up to 7 wt%, but the barrier to applications is the slow hydrogen sorption rate of the bulk material. However, making nanostructured Mg speeds up the sorption process by an order of magnitude. Neutron diffraction has been used to explore the microscopic processes that occur during hydrogen sorption, and has given detailed information on the hydrogen position and concentration in various crystallographic phases of the nanostructured material.

In addition to the use of nanostructured Mg for hydrogen storage, employing a finely dispersed catalyst like Nb or V increases the hydrogen sorption speed by another factor ten while also lowering the sorption temperature by about 50 K. Overall, this brings forward applications with total sorption speeds of minutes and with a more accessible temperature range (i.e. between room temperature and 300 °C).

In order to understand the detailed chemical mechanisms involved during the hydrogen/deuterium loading and unloading, we have undertaken an in-situ neutron diffraction study of nanostructured and catalysed Mg samples. These were prepared by mechanical alloying of pure magnesium hydride and pure niobium metal particles (4 mole %) for several hours. A constant temperature of 300 °C was used and pressures between 0 and 11 bar were applied using special sample containers and other equipment supplied by the ISIS technical team (Dreyer et al.). Fig. 1 shows typical diffraction patterns obtained with 3 minutes of counting time during desorption of D_2 gas (1 bar, 15 °C) at a rate of ~5 ml/min. The picture emerging from the analysis is extremely valuable and much more complex than originally thought.

First, a quantitative phase analysis (Rietveld refinements) reveals the coexistence of several crystalline phases: the main ones are magnesium metal and/or magnesium deuteride (hydride), coexisting with smaller fractions of magnesium oxide (2 mole %), and niobium hydride (3%). In addition, a few distinct diffraction peaks indicate the presence of a fifth phase that appears to be a cubic $(Mg,Nb)O_3$ perovskite (0.7%).

Beyond this, the large collection of time-resolved diffraction patterns allows loading/unloading process to be accurately tracked. The lattice parameter of magnesium shows clear signs of interstitially dissolved hydrogen that depends on the hydrogen gas pressure (interstitial hydrogen in metals is known to expand the lattice with 2-3 $Å^3$ per atom). During gas loading the pressure is around 5 Bar, while it is reduced gradually to around 2 Bar during desorption. In fig. 2 one can also observe that an initial super-saturation of the Mg lattice is necessary to initiate the nucleation of the hydride phase.

The magnesium deuteride phase shows an unexpectedly low deuterium concentration (as low as $MgD_{1.2}$) during the first stages of absorption and the last stages of desorption. This finding suggests that there is a significant fraction of deuterium-deficient hydride at the interface with the Mg
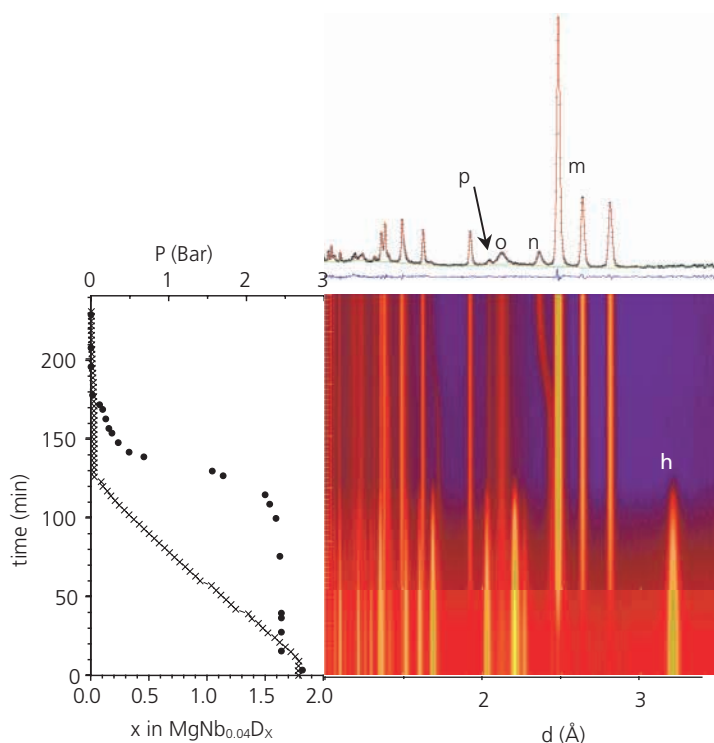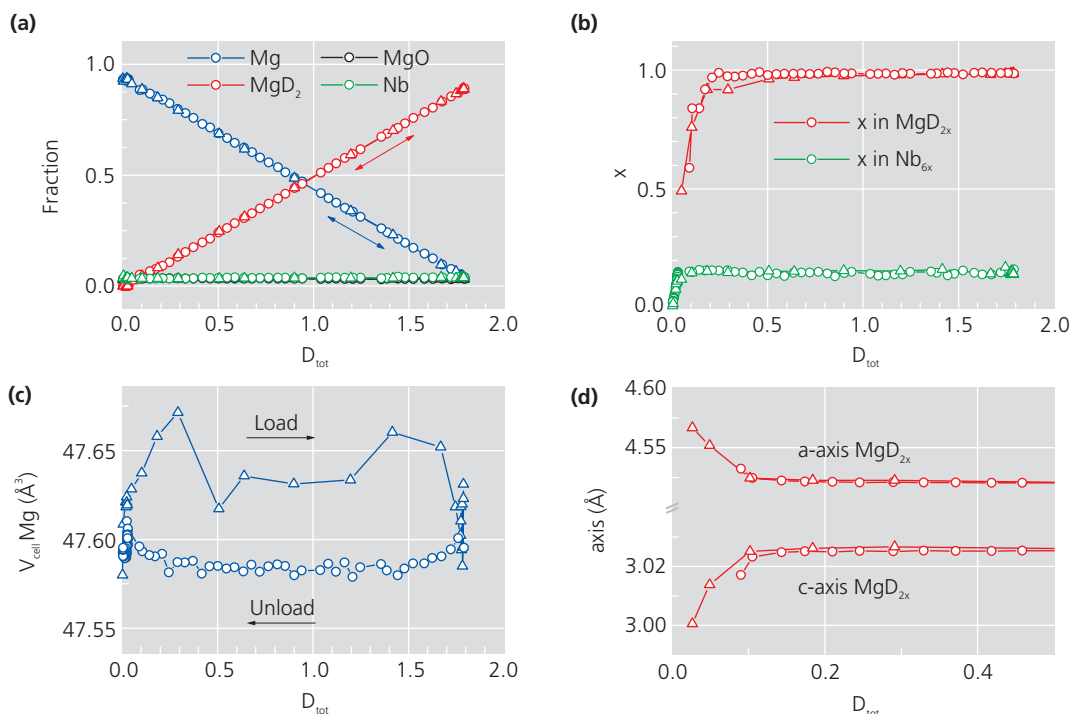

Fig. 1
Right: *GEM diffraction patterns (color coded) measured during desorption of deuterium from $MgNb_{0.04}D_2$. The time dependence of the overall D content and pressure during the experiment are shown on the left. The pattern of the fully dehydrided (**h**) material is shown on top (magnesium (**m**), niobium (**n**), MgO (**o**) and perovskite (**p**)).*

(a)

(b)

(c)

(d)

Fig. 2

*Selected crystallographic parameters that result from the Rietveld refinements. **a)** phase fractions, **b)** D concentration in MgD_{2x} and in Nb_{6x}. **c)** Mg unit cell volume during hydrogen cycling. **d)** lattice parameters of MgD_{2x}. The sample was loaded (triangles) and unloaded (circles) during the measurement.*

phase. This could be crucial for the nucleation and growth of one phase into another and also for the hydrogen diffusion rates along these interfaces: clearly the occurrence of empty hydrogen sites speeds up the diffusion enormously.

The niobium deuteride phase is almost saturated with deuterium at all pressures (D in the tetrahedral site with concentration NbD_1). The D concentration is lowered towards zero only when the pressure is reduced below ~100 mBar. This can also be observed from the shift of the Nb diffraction peak positions.

The small concentration of the Nb-Mg perovskite phase is best visible in the patterns of the fully dehydrogenated samples. We note that this phase can only be the result of the high-energy mechanical alloying treatment, which apparently

mixed surface MgO with Nb (the remaining MgO showed no change during this experiment). As many Mg-Nb-O phases are known to catalyse (de-) hydrogenation reactions, this phase could play an important role in activating the surface of the Mg particles for hydrogen uptake.

In conclusion, the in-situ neutron diffraction has revealed three key elements. First, a super-saturated hydrogen solution of the Mg phase is needed for the hydride phase to nucleate. Secondly, during hydrogen sorption a magnesium hydride phase is present with a hydrogen concentration much below the equilibrium content and which likely speeds up the process. Finally, the presence of a $(Nb,Mg)O_3$ phase, even though in small proportions, is likely to play a second catalytic role for the Mg particles, penetrating their oxide barrier.

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