STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE

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The project focuses on studies of metal hydrides, mainly based on light-weight elements. During the last few years different so-called alanates e.g. $LiAlH_4$, $NaAlH_4$ containing up to 10 wt% hydrogen have been intensively studied. Even though these materials have been known for a long time, details about structure of the starting material and desorption products are defective. For possible applications, addition of Ti or Zr compounds effectively improves the kinetics and reversibility, but the nature of the additive is not understood; whether a solid solution is formed or there is a catalytic phase present. In addition, in-situ experiments of interstitial-type metal hydrides have also been carried out to improve understanding of hydrogenation/dehydrogenation processes.

The high-resolution experiments (BM01B) were carried out on the following samples:

(a) $NaAlH_4$, pure and doped (14 samples)
(b) In-situ experiments for $TbNiAlD_x$ and Zr_2NiD_x (11 diagrams)

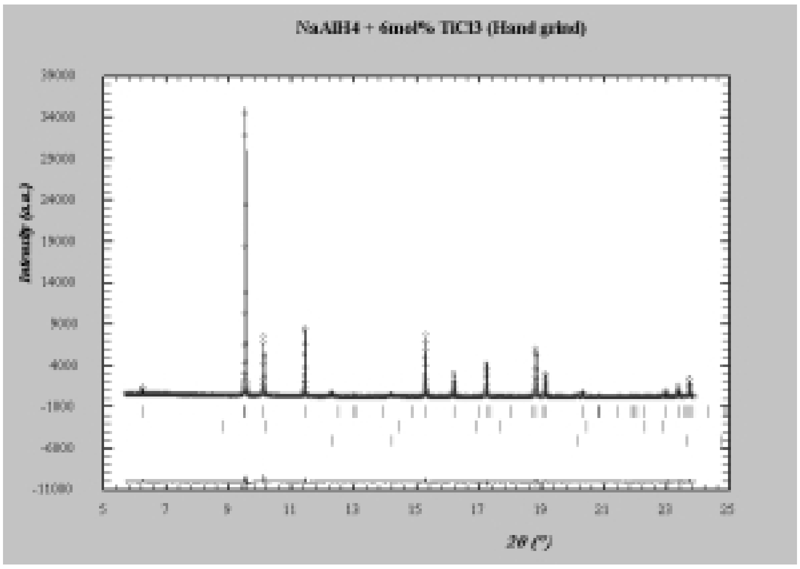
All samples were in 0.5 mm boron-glass capillaries. The wavelength was 0.50024 Å.

(a) $NaAlH_4$

$NaAlH_4$ decomposes by heating via Na_3AlH_6 + 2Al to NaH + Al. By introducing Ti additives by ball milling, this reaction is reversible at 100-150ºC at 100 bar. To understand the reason for why this additive works, it is essential to understand where the Ti is in the sample at all stages. If Ti is in a crystalline phase, synchrotron X-ray diffraction is probably the best tool to reveal the nature of Ti in $NaAlH_4$ samples.

Samples of $NaAlH_4$ with additives, Na_3AlH_6 with additives and NaH with additives were measured at BM01B. The additives tested were $TiCl_4$, $TiCl_3$ and TiF_3. Ball milling was also compared to hand grinding. The pure compounds $NaAlH_4$, $NaAlD_4$, Na_3AlH_6 and NaH were also measured for comparison, in order to detect any possible deviation in unit-cell dimensions from the pure compounds. This would be a sign of partial Ti substitution on either Na or Al position.

Rietveld refinements show that the unit-cell dimensions for $NaAlH_4$, Na_3AlH_6 and NaH are not significantly altered by Ti additives and there is no sign of a solid solution. The alteration in unit-cell dimensions for $NaAlD_4$ with $TiCl_4$ additive is also very small (0.02-0.04%). There are in addition several reflections, which are not identified yet, in some of the samples that do not originate from the pure $NaAlH_4$ system or the pure additive. A weak shoulder on the strong Al-peaks gives indications of a Ti-Al phase, but this is not yet clarified. Powder neutron diffraction has been carried out for a few selected samples. At the moment, the effect of the Ti additive could more probably be explained by a catalytic secondary phases than a solid solution. A publication describing these important results is in progress.



(b) In-situ experiments at BM01B (TbNiAlD_x and Zr_2NiD_x)

Our research group has in several years worked with these two metal hydride systems and determination of the structures as a function of hydrogen content. Our goal with these experiments was to determine the structure of saturated hydrides as a function of temperature (in vacuum). In order to increase our understanding of the desorption process and eventually to find new phases. Of particular interest is to understand the detailed structure of Zr_2Ni with high hydrogen content. The experiments were carried out at BM01B by connecting the capillary to a vacuum pump and oscillating the capillary during the experiment. The results will be combined with similar experiments with powder neutron diffraction.