Research results (Oct 2002 – Sept. 2003)

A. 1   Scientific Highlights (first 12 months)

In gas phase charging, Mg does not absorb below 200 °C and requires T>400 °C for desorption. Previous work including work by the Network partners indicates that kinetics of gas-phase sorption and electrochemical H charging/discharging are enhanced when Mg and Mg alloys are pre-milled in order to reduce grain size to submicron or nanometer range.

Addition of metallic nanoparticles such as Ni, Ti, V, Cr, Nb and others have been shown to improve sorption kinetics in of H_2 in nanostructured Mg to varying degrees (Hydro-Quebec 1999).

The GKSS partner has succeeded in further reducing absorption and desorption times in Mg at 300 C (and hydrogen pressure of 8 bars) down to a few minute by the introduction of less than 1 mole% of selected oxides.

In F-treated hydrides, a thin fluoride compound layer improves activation characteristics and avoids pyrophoricity (Japanese patents Kogakium University, Tokyo) . Avoiding the procedures of this patent, the INPG partner has used a redox-type reaction to introduce fluoride atoms along with metal catalyst particles into nanostructured MgH2-based composites.

The scientific highlights of the first 12 months of the Network research concern a better understanding of the above catalytic effects.

MgH2 with oxide catalyst Nb2O5 nanoparticle additions:

As described in the technical annex of the Network project, oxide catalysts such as Nb2O5 are less stable than magnesia (MgO).
The question is raised therefore as to their stability during hydrogen charge/discharge cycling.

If the oxide catalyst is reduced to its metallic component (Nb2O5 => Nb) accompanied by some Mg oxidation, then this type of MgH2 with oxide catalysts become nearly the same as the other type of MgH2 when metals such as Nb are added as nanoparticle catalysts directly.
The joint work during this 1st year of the Network seems to support this hypothesis but leaves other issues still unresolved.

The ESRF partner have obtained in-situ data on the evolution of the phase-distribution in the GKSS samples (2 mol% Nb2O5) during H-desorption in a monochromatised synchrotron beam diffracting in transmission. The results are presented in the next figures.
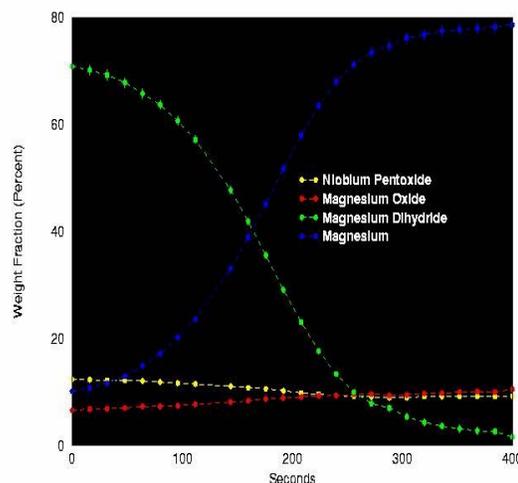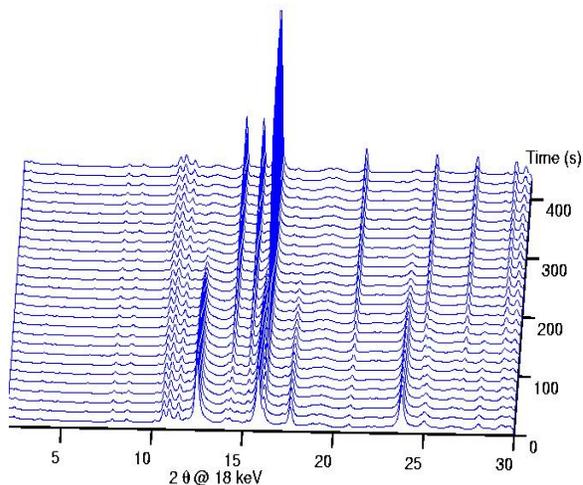
A decrease in the amount of Nb2O5 and an increase of MgO during the desorption is detected as can be seen in the figure on the right hand side for desorption at 335 C. There is certainly a decrease in the crystallinity of the former (and possibly an increase in lattice parameter) which implies that it is being attacked. In that case the oxygen from the MgO comes from the Nb2O5, and there should be either Nb metal and/or a less oxygen rich Nb oxide. There is no clear evidence for either although it would be hard to spot, in particular, the Nb due to peak overlap. Other samples (about 10 in all) heated in-the-beam in different ways show the same sorts of behaviours.

ICMSE-Sevilla has analysed structural evolution of Mg/MgH2 with 2at.% Nb2O5 nanoparticles from the GKSS partner using high-resolution transmission electron microscopy (HRTEM) together with energy-dispersive x-ray microanalysis (EDX). Evidence for Nb2O5 reduction to Nb was obtained from EDX and selected area electron diffraction patterns. Thus it is clear that at least some of the Nb2O5 cataylist is converted to Nb metal with nearly equal catalytic potency during H-cycling.

Independent results from GKSS indicate that when Nb2O5 catalyst particles are added to MgH2, the catalytic effect continues to increase up to 0.5 mole% of Nb2O5 but further addition to for example 2% Nb2O5 does not result in further improvement of sorption kinetics indicating that beyond the 0.5%, the incremental potency of Nb2O5 is reduced.

The above results suggest further consideration of at least two hypotheses:

a) Like any chemical reaction, the reaction $5Mg + Nb_2O_5 \rightleftharpoons 5MgO + 2Nb$ has an equilibrium constant and leads to an equilibrium distribution of Mg, Nb2O5, Nb and MgO at any temperature and constant O2 partial pressure. It may be, that in presence of say 5 mole% of MgO (nearly always present in Mg powders), the equilibrium content of Nb2O5 reaches about (the measured optimum) 0.5%, an amount that would not be further reduced.

b) If the Nb2O5 oxide particles can be milled down to a size of say 10 nm and the MgH2 grains milled down to a size of 25 nm, a random dispersion of 0.5% of the former in the latter would produce a nanostructure in which "on-the-average", each MgH2 nanograin would interface with a Nb2O5 nanoparticle and further addition of Nb2O5 would be less effective catalysis of H-sorption as observed.

These hypotheses will be examined shortly. The ICMSE partner has also used X-ray photo-electron spectroscopy (XPS) to examine MgH2 with Nb2O5 addition and some of the results are presented in the next figure. It can be seen that Nb2O5-addition strongly modifies the 2p line of Mg and the 1s line of oxygen.
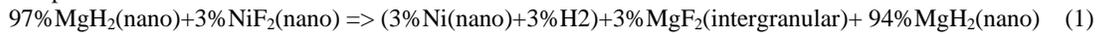
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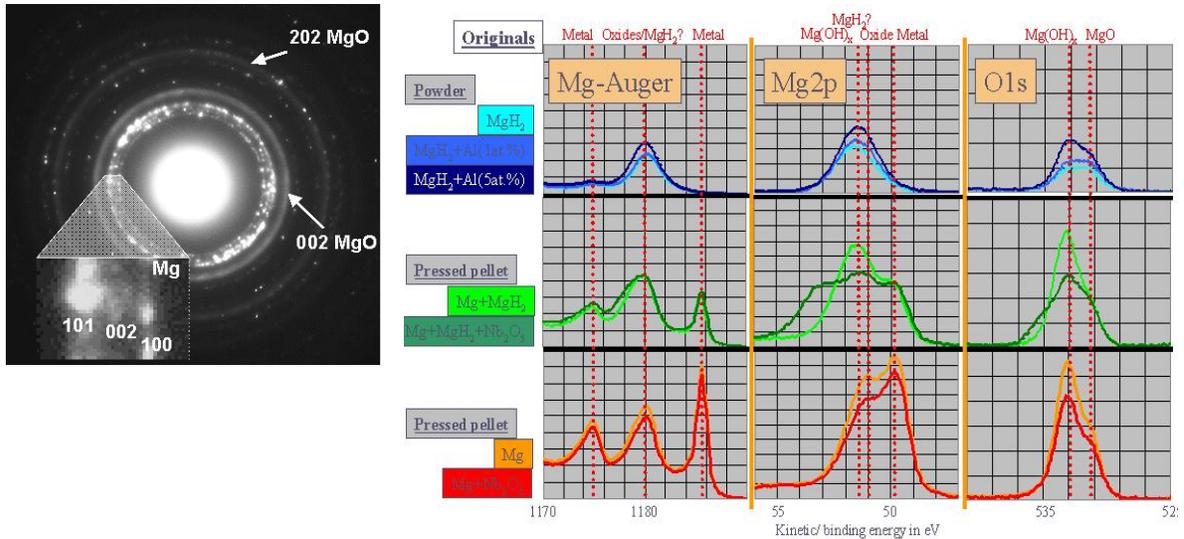
While these modifications are not fully understood, they evidence a possible key role of hydroxide groups [Mg(OH)x]. XPS is expected to be highly useful for the continuation of the Network research.
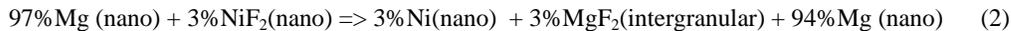
The INPG team has introduced an original fluorination process for MgH2 composites containing transition metal nanoparticles such as Fe and Ni. The procedure's objective is to generate the transition metal nanoparticles by a fluoride transfer reaction from the TM-F_x to Mg to form protective intergranular MgF_2 and a fine nanoparticle dispersion of the TM growing on the Mg or MgH_2 particles involved in the reactions.

Instead of adding Fe or Ni nanoparticles to MgH2 as in the Hydro-Quebec process, FeF3 or NiF2 nanoparticles are added through mechanical milling.

Since the per-atom heat of formation of MgF_2 is more negative than that of TM-F_x., this process, when applied to commercial TM-F_x fluorides of transition metals (TM) used in the Hydro-Quebec and GKSS processes, is expected to lead to the following redox-type reaction during the milling or at the latest during heating of the composite:

$$97\%MgH_2(nano)+3\%NiF_2(nano) => (3\%Ni(nano)+3\%H_2)+3\%MgF_2(intergranular)+ 94\%MgH_2(nano) \quad (1)$$

or

$$97\%Mg (nano) + 3\%NiF_2(nano) => 3\%Ni(nano) + 3\%MgF_2(intergranular) + 94\%Mg (nano) \quad (2)$$

Commercial-grade MgH2 and FeF3 are first milled separately for grain refinement to nanograin regime of grain size to about 10 nm. The two powders are then mixed in selected proportions (usually with 0.5 to 5 mole% FeF3) and milled together for mechanical alloying.

The transmission electron microscope images below, of the resulting powder (bright field (left) and dark field (right)) show typical grain size after mechanical alloying with average grain size in the composite seen to be about 10 nm or less.
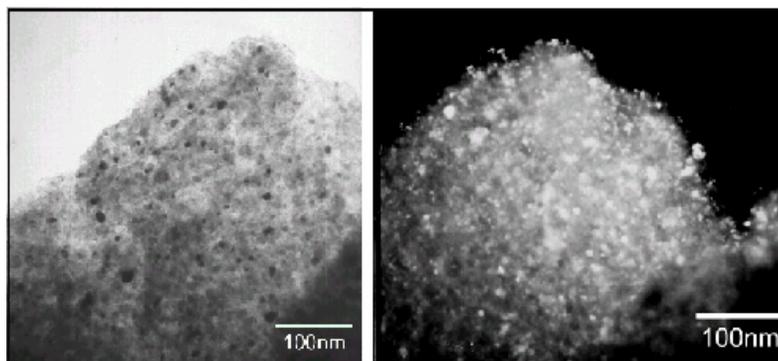

In order to compare the sorption kinetics of the Hydro-Quebec and the GKSS type powders with those of the present process, comparative differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

were performed on several powders including mechanically milled nanocomposites of $MgH_2+5\%Fe$, $MgH_2+2\%Nb_2O_5$ and $MgH_2+3\%FeF_3$ all at the same heating rate of 10 K/min.

The DSC curves on the right, regroup the behavior of all four powders (in arbitrary units). This figure clearly shows that when MgH2 is milled together with a few % transition metal fluoride (FeF3) as proposed in the INPG process, the sorption temperature is lowered by 50 C or more compared to MgH2 milled with addition of the transition metal itself (Fe) as in the Hydro-Qeubec invention or with transition metal oxide (Nb2O5) (note that in the range 225 to 275, significant desorption activity occurs only in the fluorinated powder).
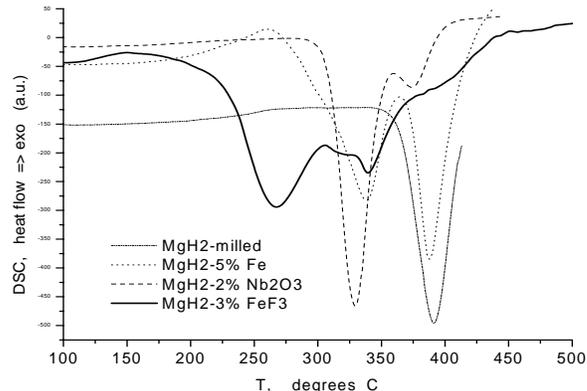
This lowering of H-sorption temperatures by 50 C in MgH_2 can be a critical step towards the development of a new family of application-enabled Mg-based composite hydrides for energy storage and transport but the behavior of the new nanocomposites has not yet been tested in cycling. The GKSS partners will undertake this task. Furthermore, the magnetic moment of the Fe (or Ni) catalyst atoms of the nanocomposites during heating is rather complex, as shown in the magnetisation measurements of the next figures. Thus further work and several publications on the new process are planned.
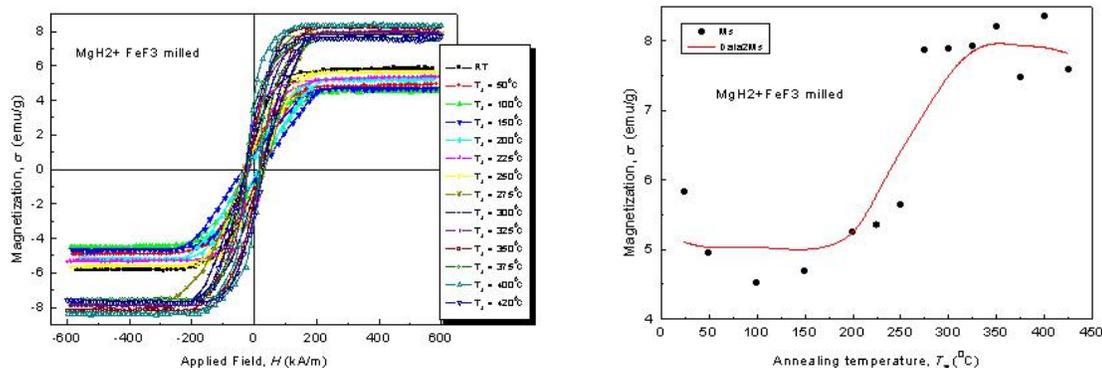
At the UAB-Barcelona, hydrogenation under milling and the catalytic role of the transition metal catalysts (Ni) was examined and compared for example to Al addition using X-ray diffraction, Differential scanning calorimetry (DSC) and Thermo-gravimetry (TG) analysis. From the diffraction patterns a full profile fitting procedure, based on the Rietveld method, was applied in order to obtain information about the microstructure parameters, such as crystallite size and microstrain, and phase fractions. It was confirmed that partial substitution of Ni with Al does not improve the behavior under milling. UAB samples were also examined at the GKSS (Hamburg) and ESRF (Grenoble).

At the facilities of the ILL-partner, small-angle neutron scattering (SANS) experiments as well as measurements in the Laue diffuse scattering region were performed on samples from the GKSS and the INPG. These experiments examine the nanocomposite evolution during in-situ H-desorption by heating in the neutron beam under vacuum of 10^{-5} bar. The data was collected using 4.54 Å wavelength in the 0 - 2.6Å^{-1} Q range before and during heat treatment between 200-400°C at various wave-vectors.

Typical results are presented (before heating-BHT and after heating AHT) in the next figures. The very large incoherent scattering length of H-atoms for neutrons (right hand side) indicated that the Laue-diffuse scattering background can be used as a quantitative tool for the study of kinetics of hydrogen sorption but the SANS data (left figure) have not yet revealed any striking novelties.
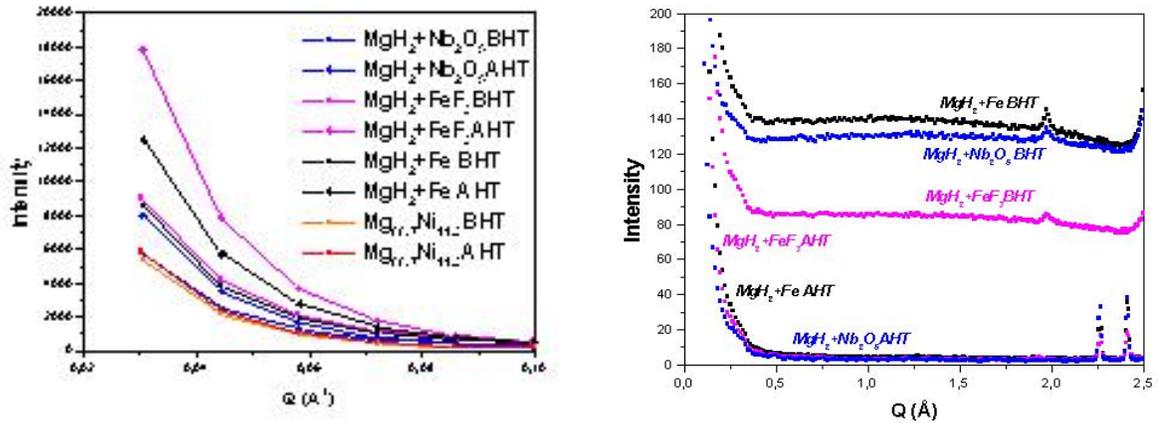
Electrochemical hydrogen insertion and cycling:

This activity performed by the Electrochemical Task Force IV has so far underlined the highly sensitive behavior of Mg-based powder electrodes in the electrolyte environment.

At the INPG, these Magnesium composites are shaped into plastified electrodes. The presence of a polymeric binder loaded with carbon black as electronic conductor, is necessary to protect the alloy against corrosion by KOH, to compensate the large volume variations during insertion-desinsertion of hydrogen and to ensure the permanence of electrical contact between alloy particles. Electrochemical insertion-desinsertion (or charge-discharge) of hydrogen is driven under potentiostatic control by a McPile multi channels microprocessor potentiostat-galvanostat device. It allows to sweep slowly the potential with a scan rate of 10mV/2hours roughly equivalent to a charge regim of C/100, step by step while recording the dynamics of the intercalation during each potential level. It is well adapted to follow the low kinetics of intercalation process of an ion/electron couple in a host matrix, in which the ionic diffusivity is several orders of magnitude smaller than in the liquid state. Cyclic voltamogram (<I>(V) curves) are drawn in plotting for each potential step the average intensity of the reduction current in the potential range explored: from Ueq to –1.2V (versus Hg-HgO reference electrode) and from Ueq to 0.4V for oxidation process. Variations of x ,the insertion (dis-insertion) rate are also drawn versus potential. These x (V) curves allow to determine the capacity delivered at each redox cycle. Theoretical capacity is determined at the beginning of the reaction from the weight and "molecular mass" of the alloy.

While the results are at best preliminary, the figure on the right shows the capacity values recovered during charge and discharge that broadly neighbor 300 mAh.g^{-1} for a composite $Mg_{88.7}Ni_{11.3}+Nb$. These values are of the order of those of the more reproducible rare-earth-Ni-based commercial metal hydrides.
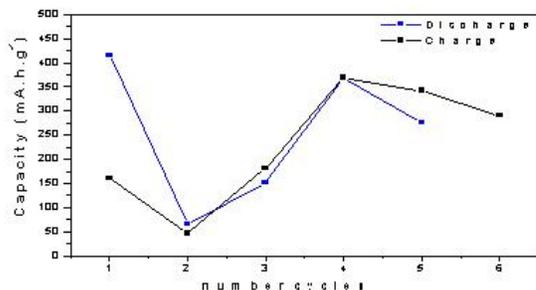
The Sofia partner has performed electrochemical studies with electrodes prepared with Mg alloy + Ni powder (1:2) + 10% water solution of PVA or Mg alloy + graphite + Teflon (emulsion) under pressures of 100-200 bars. H-absorption peak in the cathodic range, followed by H_2-gas release, H-desorption peak(s) in the anodic range and the influence of temperature on the H absorption/desorption behavior were studied. Hydrogen insertion capacity was found to be low and attributed to alloys surface passivation, slow kinetics and low stability of the hydride. Electrode preparation optimization and fluorination are planned for improvements.

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At Dortmund, the use of nanocrystalline Mg powder without and with 2 mol% Nb_2O_5 catalyst as an electrode material for electrochemical hydrogen charging processes in a 6M KOH electrolyte were studied. TEM investigation of the dehydrided Mg powder with and without catalyst showed still nanocrystalline MgH_2 in the Mg matrix and Nb_2O_5 with a grain size of about 100 nm. A strong influence of the compaction parameters and the current density but no influence of the catalyst on the hydrogenation behavior was observed. However, a strong influence of the catalyst on the hydrogen overpotential was observed and is assumed to result into a change of the electrochemical surface reaction. The addition of graphite and PTFE to the Mg/Nb_2O_5 electrodes improved the charging kinetic as well as the hydrogen content up to 1 wt.% hydrogen.

The compaction of Mg powder soluted with PTFE and graphite between a copper net for a better conductivity resulted in an electrode which could be charged only to minor hydrogen contents of 0.4 wt.% at 50 mA/g and room temperature before failure of the material, probably due to the strong recombination reaction of hydrogen at the inner copper net.

The studies revealed a strong influence of the compaction parameters and the current density but no influence of the catalyst on the hydrogenation behavior.

The influence of the compaction force (which leads to different porosity, void fraction) on the hydrogen content after 3h at 50 mA/g and room temperature is shown in the figure on the right for a Mg/Nb_2O_5-electrodes It was observed that the hydrogen content increases with less compaction force, i.e. higher porosity. Above a critical porosity the electrodes started to burn after a delay time of a few minutes.