

## **RESEARCH RESULTS (Oct 2003 – Oct 2004)**

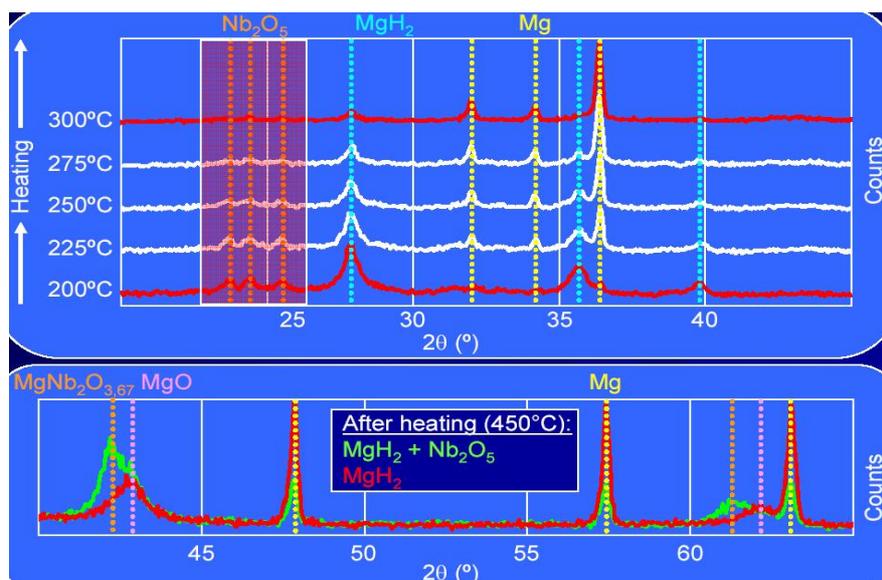
### **A.1 Scientific Highlights (second 12 months)**

First we recapitulate the highlights of Year 1.

We recall that 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 prior to the start of the present RTN indicated 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 of H<sub>2</sub> in nanostructured Mg to varying degrees. The GKSS partner had 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. The INPG partner had used a redox-type reaction to introduce fluoride atoms along with metal catalyst particles into nanostructured MgH<sub>2</sub>-based composites.

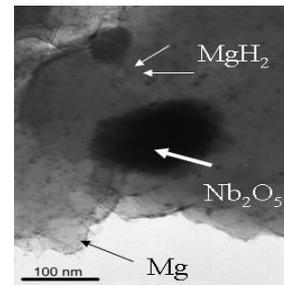
As described in the technical annex of the Network project, oxide catalysts such as Nb<sub>2</sub>O<sub>5</sub> are less stable than magnesia (MgO). The question was raised therefore as to their stability during hydrogen charge/discharge cycling. If the oxide catalyst is reduced to its metallic component (Nb<sub>2</sub>O<sub>5</sub> => Nb) accompanied by some Mg oxidation, then this type of MgH<sub>2</sub> with oxide catalysts would become nearly the same as the other type of MgH<sub>2</sub> nanocomposites with metals such as Nb added as nanoparticle catalysts directly. Examining this type of reaction using synchrotron radiation and high resolution TEM as well as XPS and other techniques was a focus of research during the 1<sup>st</sup> year of the Network (collaborative work of four partners ESRF, GKSS, ICMSE and INPG).

ICMSE-Sevilla has now analysed structural evolution of Mg/MgH<sub>2</sub> with 2at.% Nb<sub>2</sub>O<sub>5</sub> nanoparticles prepared by the GKSS partner using high-resolution transmission electron microscopy together with energy-dispersive x-ray microanalysis (EDX). The results show the Nb-oxide particles surrounded by a layer of Mg-rich oxide. However, TEM results concern a single particle while XRD and x-ray photo-electron spectroscopy (XPS) probes a larger sample volume and the evolution of a large number of particles and are thus more reliable. The next figure shows XRD results from Sevilla proving the formation of a Nb-Mg-O mixed oxide at the Nb<sub>2</sub>O<sub>5</sub> particles' interfaces with the surrounding MgH<sub>2</sub> nano-grains

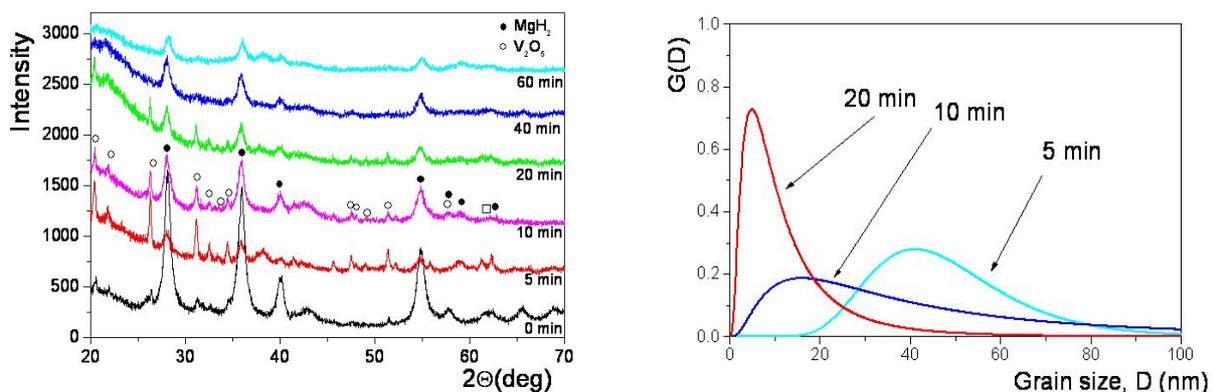


Nb<sub>2</sub>O<sub>5</sub> Bragg peaks are seen to disappear with heating together with the appearance of Bragg peaks of a phase identified as MgNb<sub>2</sub>O<sub>3.67</sub>.

The TEM image on the right (obtained by the Dörtmund team) on the same GKSS powder also shows appearance of an interfacial reaction layer around a Nb<sub>2</sub>O<sub>5</sub> particle.



During the second year, the Sofia team performed XRD investigation of MgH<sub>2</sub> milled with nanoparticles of another mixed valence metal oxide catalyst (V<sub>2</sub>O<sub>5</sub>) isostructural to Nb<sub>2</sub>O<sub>5</sub>. The figure below shows on the left hand side the disappearance of V<sub>2</sub>O<sub>5</sub> Bragg peaks during milling and on the right, the V<sub>2</sub>O<sub>5</sub> nano-particle size evolution before disappearance. Since no new peaks come to replace the disappearing V<sub>2</sub>O<sub>5</sub> Bragg peaks, it is thought that particles become amorphous or form an amorphous mixed oxide with Mg.



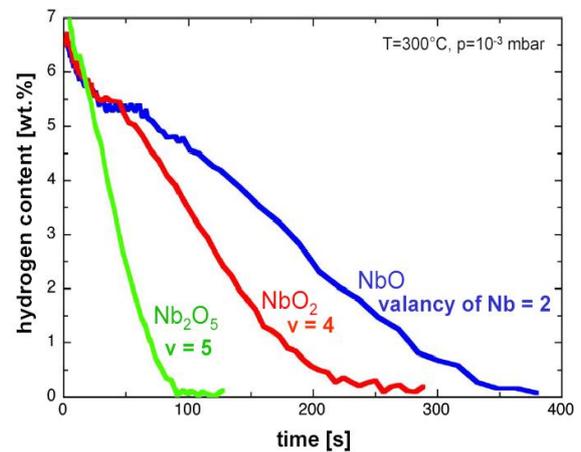
Second year results from GKSS indicate that when Nb<sub>2</sub>O<sub>5</sub> catalyst particles are added to MgH<sub>2</sub>, the catalytic effect continues to increase up to 0.5 mole% of Nb<sub>2</sub>O<sub>5</sub> but further addition to for example 2% Nb<sub>2</sub>O<sub>5</sub> does not result in further improvement of sorption kinetics indicating that beyond the 0.5%, the incremental potency of Nb<sub>2</sub>O<sub>5</sub> is reduced.

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

- Like any chemical reaction, reactions such as  $5\text{Mg} + \text{Nb}_2\text{O}_5 \rightleftharpoons 5\text{MgO} + 2\text{Nb}$  or  $\text{Mg} + \text{Nb}_2\text{O}_5 \rightleftharpoons \text{MgNb}_2\text{O}_x$  have equilibrium constants and lead to an equilibrium distribution of Mg, Nb<sub>2</sub>O<sub>5</sub>, Nb and MgO or MgNb<sub>2</sub>O<sub>x</sub> at any temperature and constant O<sub>2</sub> partial pressure. It may be, that in presence of say 5 mole% of MgO (nearly always present in Mg powders), the equilibrium content of the Nb oxide reaches about 0.5% (the measured optimum), an amount that would not be further reduced and a mixed valence state of Nb would be established at the interfaces of the partially reduced Nb-oxide nanoparticles.
- If the Nb<sub>2</sub>O<sub>5</sub> oxide particles can be milled down to a size of say 10 nm and the MgH<sub>2</sub> 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 MgH<sub>2</sub> nanograin would interface with a Nb<sub>2</sub>O<sub>5</sub> nanoparticle and further addition of Nb<sub>2</sub>O<sub>5</sub> would be less effective in catalysis of H-sorption as observed.

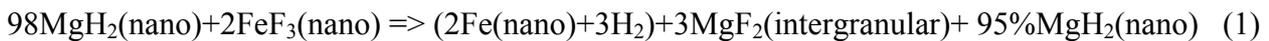
## H-sorption in Mg

As can be seen in the figure on the right (second year results from the GKSS), the catalytic potency of Nb-oxides increases in going from NbO to NbO<sub>2</sub> to Nb<sub>2</sub>O<sub>5</sub>. This result seems to support hypothesis a) above.



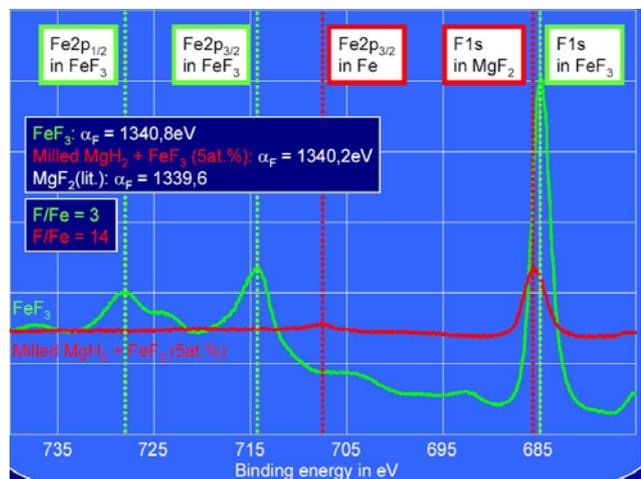
The INPG team had introduced an original fluorination process for MgH<sub>2</sub> composites containing transition metal (TM) nanoparticles such as Fe and Ni. The procedure generates the transition metal nanoparticles by a fluorine transfer reaction from the TM-F<sub>x</sub> to Mg to form protective inter-granular MgF<sub>2</sub> and a fine nanoparticle dispersion of the TM growing on the Mg or MgH<sub>2</sub> particles involved in the reactions.

Since the per-atom heat of formation of MgF<sub>2</sub> is more negative than that of TM-F<sub>x</sub>, this process, when applied to commercial TM-F<sub>x</sub> 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:



To what extent the fluorine transfer from Fe to Mg and generation of Fe nanoparticles occurs during milling or the first heating cycle depends in part on the milling conditions (details of energy transfer from milling ball(s) to the milled powder)

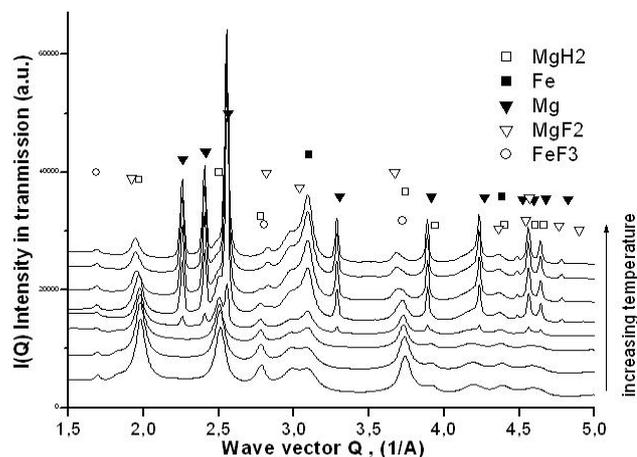
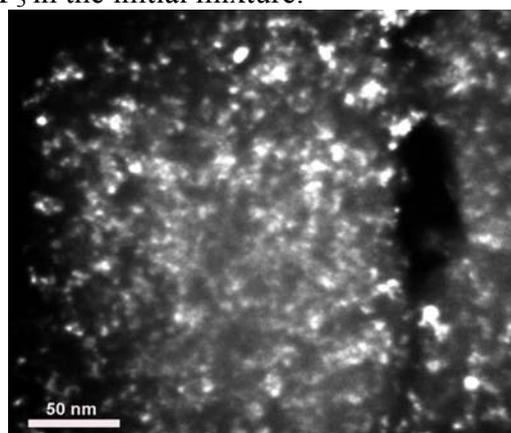
While this detail is not relevant for subsequent heating (gas phase H-charge-discharge cycles) and potential applications in gas phase, demonstration of the occurrence of the transfer reaction itself is essential and has now been proven (second year) both by in-situ XRD results from the ESRF and by XPS data from Sevilla. The figure on the right shows the evolution of the XPS spectra in MgH<sub>2</sub>+FeF<sub>3</sub> powders of INPG obtained recently in Sevilla. The disappearance of the Fe2P<sub>1/2</sub>, Fe2P<sub>3/2</sub> and F1s peaks from FeF<sub>3</sub> and appearance of the F1s peak from MgF<sub>2</sub> and a weak Fe2P<sub>3/2</sub> peak from emerging Fe particles is clearly observed.



The next figure presents a typical dark-field TEM image (on the left) of an as-milled MgH<sub>2</sub>+3%FeF<sub>3</sub> composite obtained using the (first) diffraction ring corresponding both to the (200) reflection of β-MgH<sub>2</sub> and the (111) reflection of MgF<sub>2</sub>. The particle sizes, measured from the dark-field images were mostly within the range of 5 to 10 nm.

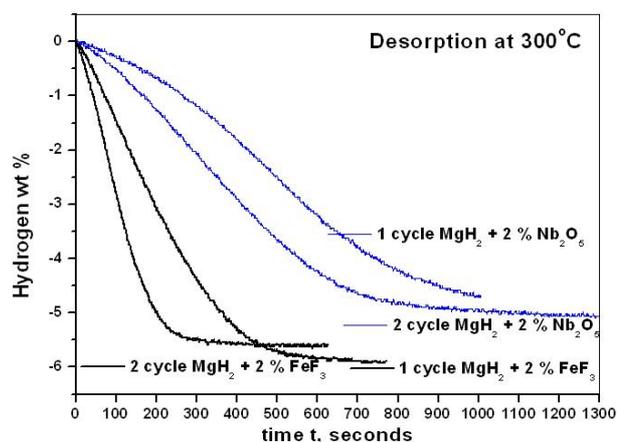
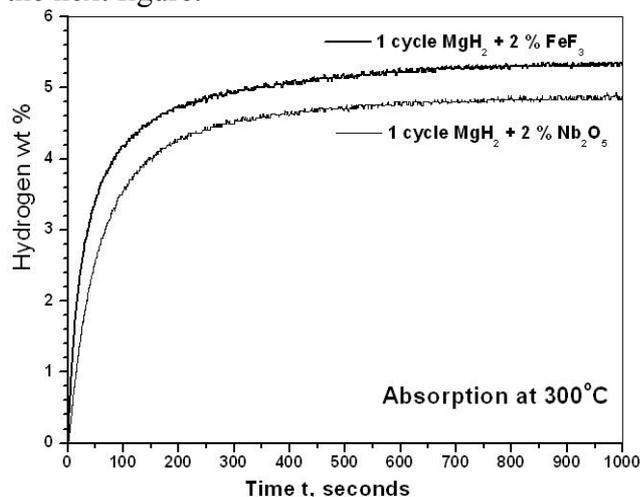
Depending on the milling conditions a partial fluorine transfer reaction of the type of Eq. (1) is induced in this powder, forming protective intergranular MgF<sub>2</sub> and a fine nanoparticle dispersion of Fe in the Mg or MgH<sub>2</sub> powder.

The synchrotron XRD patterns of the as-milled composite (second year work at ESRF, next figure, right side) indicates presence of the following phases: tetragonal  $\beta$ -MgH<sub>2</sub>, MgO, FeF<sub>3</sub>, Fe and Mg (next figure right side). The appearance of Fe thus indicates that some degree of transfer of F from FeF<sub>3</sub> to MgF<sub>2</sub> occurred during the milling. An increase in the intensity of the Fe peaks and a decrease in the intensity of the FeF<sub>3</sub> peak are observed in the synchrotron XRD pattern at higher temperatures (same figure). This indicates that the fluorine transfer reaction is then completed during the first heating. The presence of MgF<sub>2</sub> could not be clearly detected by XRD due to its low volume and electron density although a small shoulder on the left side of the first MgH<sub>2</sub> peak may suggest its presence. However, XRD peaks of MgF<sub>2</sub> appeared after milling with large quantities of FeF<sub>3</sub> in the initial mixture.



Comparison of sorption kinetics of the Hydro-Quebec and the GKSS type powders with those of the present process were previously performed and reported using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Subsequent to our Year 1 report, Sievert charge-discharge cycles were performed on mechanically milled nanocomposites of MgH<sub>2</sub>+2%Nb<sub>2</sub>O<sub>5</sub> and MgH<sub>2</sub>+3%FeF<sub>3</sub>.

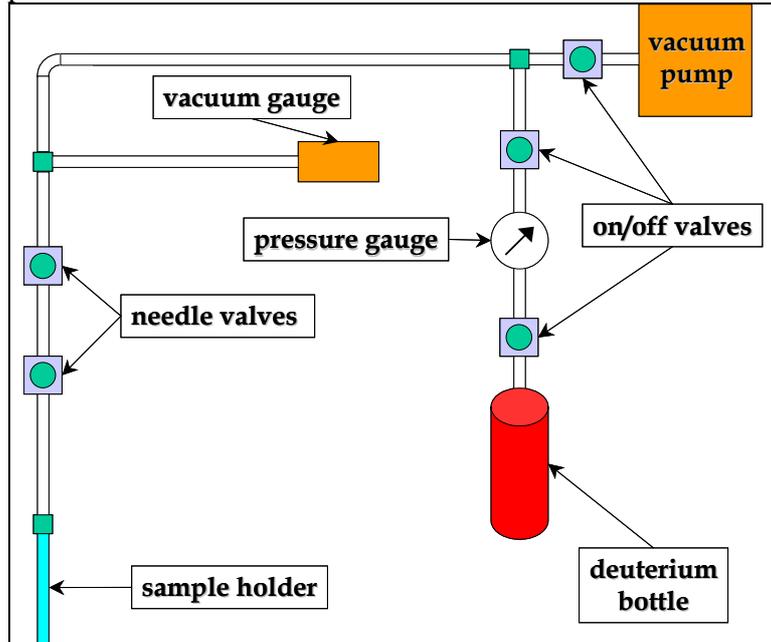
The DSC curves in the Year 1 report and the Midterm report clearly showed that when MgH<sub>2</sub> is milled together with a few % transition metal fluoride (FeF<sub>3</sub>), the sorption temperature is lowered by 50 C or more compared to MgH<sub>2</sub> milled with addition of the transition metal itself as in the Hydro-Québec invention or with transition metal oxide (Nb<sub>2</sub>O<sub>5</sub>). Since then the Network has compared desorption kinetics of MgH<sub>2</sub> nanocrystalline powders containing FeF<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> prepared at the INPG and tested during cyclic charge-discharge at the GKSS at 300C as shown in the next figure.



While the FeF<sub>3</sub> containing powder is not yet optimised, the H-sorption kinetics are clearly seen to be twice as fast as in the powders containing Nb<sub>2</sub>O<sub>5</sub>. FeF<sub>3</sub> containing MgH<sub>2</sub> powder now appears to be capable of the fastest H-sorption kinetics known to date in MgH<sub>2</sub>-based powders at 300°C (in 200 seconds) and improves with cycling.

This type of gas-phase charge-discharge experiment can now be performed in the beam at the ILL and ESRF partner facilities using an apparatus designed and built under supervision of Dr G. Vaughan of the ESRF team and subsequently modified by the INPG.

The apparatus was then used by several Yrs (M. Venstrom-ESRF, S. Deledda-INPG A. Borisova-INPG) at the ILL neutron beam line D16 supervised by Dr G. Fragneto of the ILL using deuterium instead of hydrogen to avoid incoherent scattering as observed in the Year 1 experiment with H<sub>2</sub>. Some results recently prepared by S. Deledda and M. Venstrom will now be presented: The next figure shows the set up that was developed in order to perform in-situ hydrogen desorption and absorption. The powders were heated in situ by means of a gas blower (not shown in the figure) to temperatures of up to 350 °C.



The powders investigated at the ILL consisted of ball milled MgH<sub>2</sub> composites containing either different amounts of Nb<sub>2</sub>O<sub>5</sub> or FeF<sub>3</sub> produced at the GKSS and INPG. In this report results for ball milled MgH<sub>2</sub> + 5 mol.% FeF<sub>3</sub> powders are going to be presented.

### Small Angle Neutron Scattering (SANS)

SANS results showed that for  $0.02 \text{ \AA}^{-1} < q < 0.2 \text{ \AA}^{-1}$  the scattered intensity  $I(q)$  obeys a power law, which can be described by the equation

$$I(q) = I_0 q^{-\alpha}$$

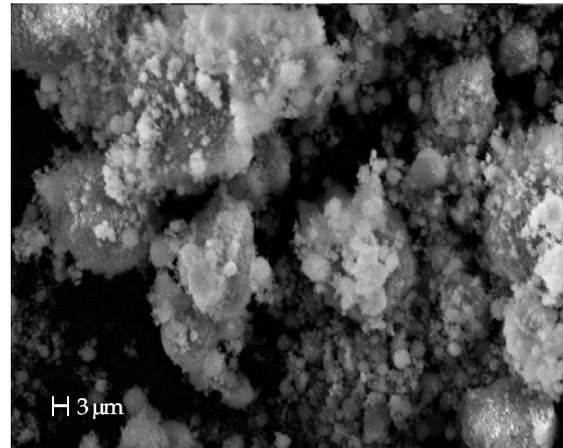
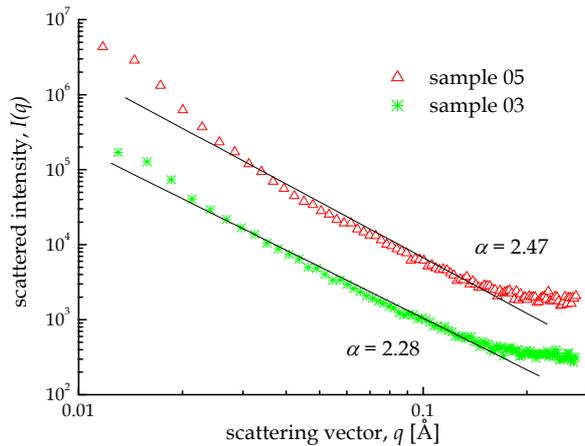
where  $\alpha$  and  $I_0$  are constants. The magnitude of the exponent  $\alpha$ , which can be evaluated by a linear fit of the  $\log(I(q))$ - $\log(q)$  relation, can give information on the nature of the structure producing the scattering. For instance, if  $\alpha = 4$  then Porod's law

$$I(q) = 2\pi I_e \delta^2 S q^{-4}$$

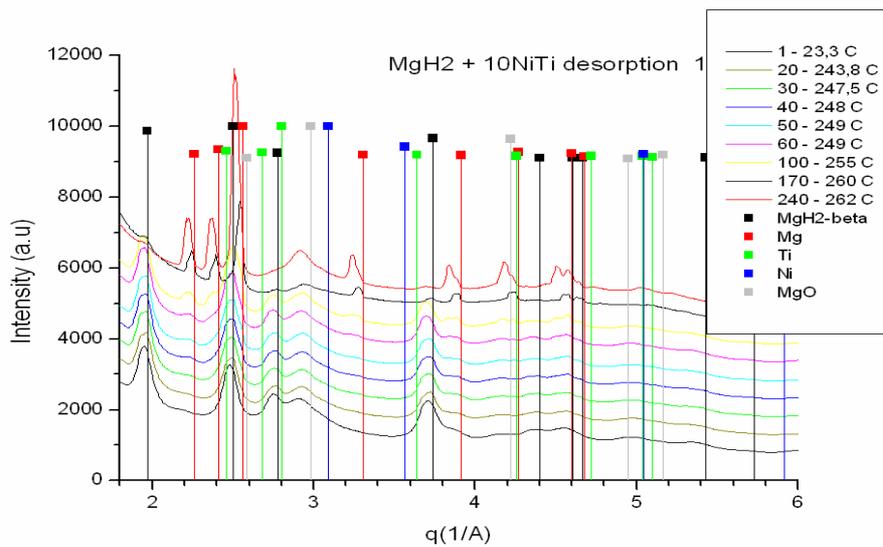
is satisfied, indicating that scattering results from randomly oriented scattering elements with a sharp smooth boundary surface.  $\delta$  is the difference of the scattering-length density of the scatterer and the surrounding medium,  $S$  is the internal surface of the scatterer, and  $I_e = 1$  for neutrons.

The next figure (left hand side) shows the room-temperature neutron small-angle scattering SANS curves for two different batches of ball-milled MgH<sub>2</sub> + 5 mol.% FeF<sub>3</sub> composite powders. The power-law regime is easily recognized for  $0.02 \text{ \AA}^{-1} < q < 0.15 \text{ \AA}^{-1}$ . Within this range, a linear fit yields a power-law scattering exponent of about 2.3/2.45, which is well below the value expected for Porod's law. Such kind of positive deviation from Porod's law is usually observed when the scattering entity is a mass fractal or a surface fractal. It is likely that such a fractal structure stems from the powder particle aggregates which usually result after ball milling. Typical powder particle aggregates can be observed in the accompanying SEM picture of as-milled MgH<sub>2</sub> powders (next

figure, right side). Self-similarity features, which are characteristic of fractal structures, can be observed.



Finally, the modified version of the in-the-beam gas charge-discharge apparatus was used on the ID11 beamline at the ESRF. Sorption kinetics in a number of new MgH<sub>2</sub> milled nanocomposites containing the following new catalysts in nanoparticle distributions were examined. These included NiNb, NiTi, FeTi and Nb+MgF<sub>2</sub>. The MgH<sub>2</sub> nanocomposite containing NiTi added catalyst proved to have the fastest hydrogen sorption kinetics. The next figure shows the results of the first desorption from MgH<sub>2</sub>+NiTi.



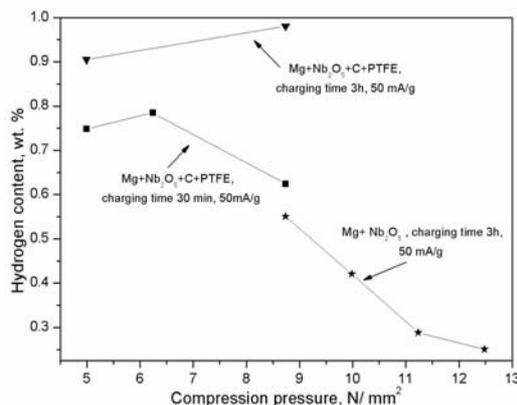
As seen by the appearance of the Mg Bragg peaks, desorption occurs in the temperature range 240 to 262 C. Further optimization of this new and promising nanocomposite is likely to lead to even faster sorption kinetics at still lower temperatures.

### Electrochemical hydrogen insertion and cycling:

The activity performed by the Electrochemical Task Force IV has firstly underlined the highly sensitive behavior of Mg-based powder electrodes in the electrolyte environment and the adverse effect of corrosion on subsequent properties of the hydride electrode

The influence of compaction with a suspension of graphite and PTFE on the capacity  $\text{MgH}_2+\text{Nb}_2\text{O}_5$ -catalyst electrodes at various compaction pressures was studied in Dortmund. It was found that that compaction with PTFE + C significantly increases H-insertion capacity as seen in the figure on the right.

Also, a strong influence of the catalyst, i.e. an increase in the hydrogen content was observed, in particular with decreasing current densities.



At the INPG,  $\text{Nb}_2\text{O}_5\text{-MgH}_2$  Hydride prepared by GKSS was shaped into thin film plastified electrode. In addition to faster kinetics, an improved corrosion resistance was observed due to the catalyst, and this was preserved during cycling by the modification of the polymeric binder formula. However, the best results were obtained with  $\text{MgH}_2$  composites containing initially  $\text{FeF}_3$  nanoparticles. With the fluoride, the storage capacity is preserved during cycling and furthermore increases linearly from  $85 \text{ mA.h.g}^{-1}$  at the first cycle to 1600 after several cycles as seen in the results presented in the figure below right.

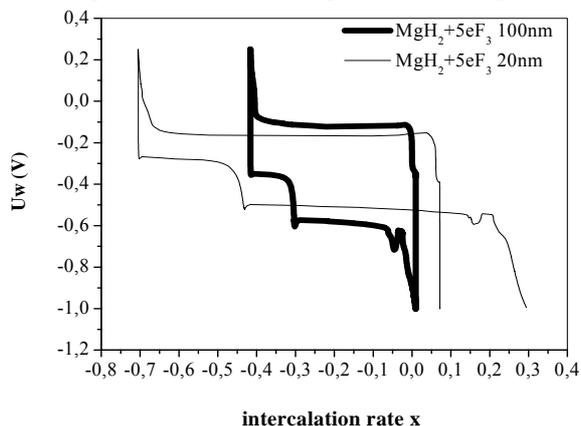


Fig.4 (V,x) curves of  $\text{MgH}_2$ ,  $\text{FeF}_3$  20nm, 100nm with 10 mA/g

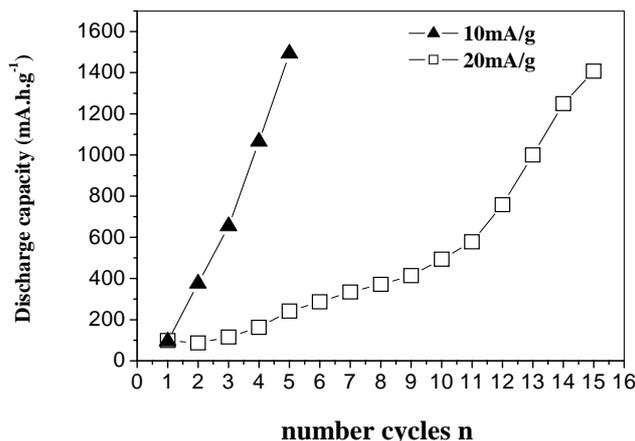


Fig. 5 ( $\text{MgH}_2$ ,  $\text{FeF}_3$ ): Variation of capacity during cycling with 10 and 20  $\text{mA.g}^{-1}$  (100nm)

Unfortunately, the voltammogram of all the studied samples recorded at  $25^\circ\text{C}$  with the same potential scan rate exhibit during reduction (charge) and oxidation (discharge) 2 peaks at  $-0.3\text{V}$  and  $-0.6\text{V}$  in charge and  $-0.4\text{V}$  and  $-0.08\text{V}$  in discharge (left side figure). The last value, at which the maximum of capacity is delivered, is too high to allow this material to be used as negative electrode in MH-Ni batteries at this time.

Thus the Network research has progressed well and better manipulation of both gas-phase and electrochemical H-charge/discharging kinetics at high capacities has been achieved and the results presented/accepted for international conferences/journals represent an advancement of the state of knowledge in this area.

## A.2 Joint Publications and Patents

### A.2.1 List of Publications with contract YRs as co-authors in *bold italique*

D. Zander (Dortmund), ***Lyudmila Lyubenova*** (Dortmund), U. Köster (Dortmund), T. Klassen (GKSS) M. Dornheim (GKSS), "Hydrogenation of Nanocrystalline Mg-based Alloys" in: "Hydrogen Storage Materials", eds. M. Nazri, G-A. Nazri, R.C. Young, C. Ping, Mat.Res.Soc.Symp.Proc. (Warrendale 2004), Vol. 801, BB 3.1

D. Zander (Dortmund), ***Lyudmila Lyubenova*** (Dortmund), U. Köster (Dortmund), M. Dornheim (GKSS), ***François Aguey-Zinsou*** (GKSS), T. Klassen (GKSS), Proc. 9th Int. Symp. On Metal-Hydrogen Systems, Cracow, Poland; J. Alloys Comp. (2004)

T. Spassov (Sofia), ***Pau Solsona*** (Sofia-UAB), S. Bliznakov (Sofia), S.Surinach (UAB), M.D.Baró (UAB), "Synthesis and hydrogen sorption properties of nanocrystalline Mg<sub>1.9</sub>M<sub>0.1</sub>Ni (M=Ti,Zr,V) obtained by mechanical alloying" Journal of Alloys and Compounds 356-357 (2003) 639-643.

T. Spassov (Sofia), ***Pau Solsona*** (Sofia-UAB), S.Surinach (UAB), M.D.Baró (UAB), "Optimization of the ball-milling and heat treatment parameters for synthesis of amorphous and nanocrystalline Mg<sub>2</sub>Ni-based alloys" Journal of Alloys and Compounds, 349 (2003) 242-254

***Pau Solsona*** (Sofia-UAB), ***Stefania Doppiu*** (UAB), T. Spassov (Sofia), S.Surinach (UAB), M.D.Baró (UAB), "Evolution of amorphous and nanocrystalline phases in mechanically alloyed Mg<sub>1.9</sub>M<sub>0.1</sub>Ni (M = Ti, Zr, V)", Journal of Alloys and Compounds (in press)

P.Delchev (Sofia), ***Pau Solsona*** (Sofia-UAB), B.Drenchev (Sofia), N.Drenchev (Sofia), T.Spassov (Sofia), M.D.Baró (UAB) "Direct hydriding of Mg<sub>87</sub>Al<sub>7</sub>Ni<sub>3</sub>Mn<sub>3</sub> by reactive mechanical grinding in hydrogen atmosphere and influence of particle size on the dehydriding reaction", Journal of Alloys and compounds (2004) submitted

***Ádam Révész*** (Sofia), ***Daniel Fátay*** (Sofia), T. Spassov (Sofia), D.Zander (Dortmund), "Influence of particle size on the H-sorption in ball milled Mg with Nb<sub>2</sub>O<sub>5</sub> as catalyst" Proc. ISMANAM 2004, J. Metastable and Nanocryst. Mater.

P.Delchev (Sofia), ***Pau Solsona*** (Sofia-UAB), B. Drenchev(Sofia), N.Drenchev (Sofia), T. Spassov (Sofia), M.D.Baró (UAB), "Direct hydriding of Mg<sub>87</sub>Al<sub>7</sub>Ni<sub>3</sub>Mn<sub>3</sub> by reactive mechanical grinding in hydrogen atmosphere and influence of particle size on the dehydriding reaction" Journal of Alloys and Compounds (2004) (submitted)

***Oliver Friedrichs*** (Sevilla), ***Lukasz Kolodziejczyk*** (Sevilla), C.López-Cartés (Sevilla), J.C.Sánchez-López (Sevilla), A. Fernández (Sevilla), M.Dornheim (GKSS), T.Klassen (GKSS), R.Bormann(GKSS), "In situ TEM and XRD Thermal Study of Nanocrystalline Mg-Based Powders for Hydrogen Storage". International Symposium on Metal-Hydrogen Systems, Fundamentals & Application, September 5-10, 2004, Krakow, to appear in the J. of Alloys & Compounds

***Marie Vennstrom*** (ESRF-ILL), G. Vaughan (ESRF) , M. Dornheim (GKSS), T. Klassen (GKSS), "Real-time detection of phase distribution during H-desorption in MgH<sub>2</sub> doped with Nb<sub>2</sub>O<sub>5</sub> nanocomposites in a synchrotron beam" Proc. 9th Int. Symp. On Metal-Hydrogen Systems, Cracow, Poland; J. Alloys Comp. (2004)

***Ana Borissova*** (INPG), Ch. Poinignon (INPG), ***Stefano Deledda*** (INPG),, A. R. Yavari (INPG), and T. Klassen (GKSS), "Electrochemical storage of hydrogen in Nb<sub>2</sub>O<sub>5</sub> and FeF<sub>3</sub> magnesium nanocomposites" MH2004 4-8 september 2004 Krakow, to appear in J. Alloys & Compounds

**Ana Borissova** (INPG), Ch. Poinsignon (INPG), **Stefano Deledda** (INPG), A. R. Yavari (INPG), W.J.Botta (INPG), T. Klassen, (GKSS), "Electrochemical storage of hydrogen in MgH<sub>2</sub> Nanocomposites" ISMANAM 22-26 august 2004 Sendai-Japan, Proc. ISMANAM 2004, J. Metastable and Nanocryst. Mater.

**Stefano Deledda** (INPG), **Ana Borissova** (INPG), Ch. Poinsignon (INPG), W.J.Botta (INPG), M. Dornheim (GKSS), T. Klassen (GKSS), "H-Sorption in MgH<sub>2</sub> Nanocomposites Containing Fe or Ni with Fluorine", MH2004 4-8 september 2004 Krakow, to appear in J. Alloys & Compounds

A. R. Yavari (INPG), A. LeMoulec (INPG), F. R. de Castro (INPG), **S. Deledda** (INPG), **O. Friedrichs** (Sevilla), W. J. Botta (INPG), G. Vaughan (ESRF), T. Klassen (GKSS), A. Fernandez (Sevilla) and Å. Kvick (ESRF) "Improvement in H-sorption kinetics of MgH<sub>2</sub> powders by using Fe nanoparticles generated by reactive FeF<sub>3</sub> addition" in press Scripta Mater.

### Abstracts

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**Oliver Friedrichs** (Sevilla), C.López-Cartés (Sevilla), J.C.Sánchez-López (Sevilla), A. Fernández (Sevilla), M.Dornheim (GKSS), T.Klassen (GKSS), R.Bormann (GKSS), "XPS and TEM Study of the Oxygen Passivation Behaviour of Nanocrystalline Mg and MgH<sub>2</sub>", 7<sup>th</sup> International Conference on Nanostructured Materials, June 20-24, 2004, Wiesbaden, Germany.

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