

Network Scientific Highlights (3rd Year and Final Report)

As we present new and final results of the Network collaborative research, we will recapitulate the previous highlights (Year 1 and Year 2) but for full details please read our previous reports on <http://www.inpg.fr/RTN-MgH2/> and still more in the Network's joint publications listed in the next section.

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 H₂ 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 MgH₂-based composites.

As described in the technical annex of the Network project, oxide catalysts such as Nb₂O₅ 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 (Nb₂O₅ => Nb) accompanied by some Mg oxidation, then this type of MgH₂ with oxide catalysts would become nearly the same as the other type of MgH₂ 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 of the Network

The ICMSE-Sevilla partner analysed structural evolution of Mg/MgH₂ with 2at.% Nb₂O₅ nanoparticles prepared by the GKSS partner using high-resolution transmission electron microscopy together with energy-dispersive x-ray microanalysis (EDX). The results showed 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) probe a larger sample volume and the evolution of a large number of particles and are thus more reliable. XRD results from Sevilla proved the formation of a Nb-Mg-O mixed oxide at the Nb₂O₅ particles' interfaces with the surrounding MgH₂ nano-grains.(see previous reports on <http://www.inpg.fr/RTN-MgH2/>).

Nb₂O₅ Bragg peaks disappeared with heating together with the appearance of Bragg peaks of a phase identified as MgNb₂O_{3.67}. The TEM images obtained by the Dörtmund team on the same GKSS powder also shows appearance of an interfacial reaction layer around a Nb₂O₅ particle.

During the second year, the Sofia team performed XRD investigation of MgH₂ milled with nanoparticles of another mixed valence metal oxide catalyst (V₂O₅) isostructural to Nb₂O₅.

Their figures presented in < 2nd Year Report (Oct 2003 - Oct 2004) > showed the disappearance of V₂O₅ Bragg peaks during milling and the V₂O₅ nano-particle size evolution before disappearance. Since no new peaks come to replace the disappearing V₂O₅ Bragg peaks, it was thought that particles become amorphous or formed an amorphous mixed oxide with Mg.

Second year results from GKSS indicated 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 suggested further consideration of at least two hypotheses:

- a) 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_2O_5 , Nb and MgO or MgNb_2O_x at any temperature and constant O_2 partial pressure.
- b) If the Nb_2O_5 oxide particles can be milled down to a size of say 10 nm and the MgH_2 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_2 nanograin would interface with a Nb_2O_5 nanoparticle and further addition of Nb_2O_5 would be less effective in catalysis of H-sorption as observed. It would also saturate any mechanical stabilisation of the nanostructure by grain-boundary pinning.

The catalytic potency of Nb-oxides was shown to increase in going from NbO to NbO_2 to Nb_2O_5 . This result seemed to support hypothesis a) above.

The INPG team had introduced an original fluorination process for MgH_2 composites containing transition metal (TM) nanoparticles such as Fe and Ni. The procedure generates the transition metal nanoparticles by a fluorine (F-transfer) reaction from the TM-F_x to Mg-F_x 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.

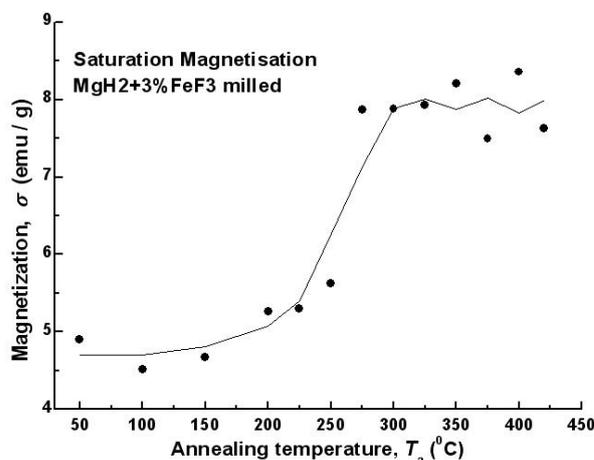
Since the per-atom heat of formation of MgF_2 is more negative than that of TM-F_x , this process, when applied to commercial TM-F_x fluorides of transition metals (TM) used in the Hydro-Quebec and GKSS processes, was expected to lead to the following redox-type reaction during the milling or at the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



To what extent the F-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).

Magnetisation measurements during heating of such as-milled powder composites showed a residual magnetisation prior to heating while FeF_3 is paramagnetic, indicating some conversion of FeF_3 to $\text{Fe} + \text{MgF}_2$ during milling.

As the temperature was increased, the magnetisation reached the expected level for the Fe content of FeF_3 in pure Fe state (see figure on the right).



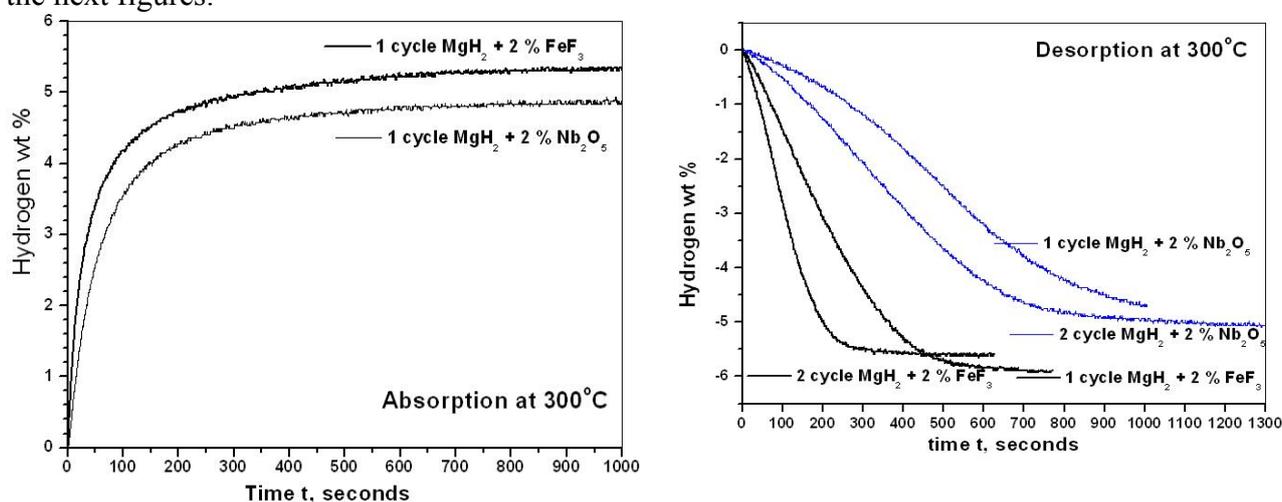
While this detail is not relevant for subsequent heating cycles (gas phase H-charge-discharge cycles) and potential applications in gas phase, demonstration of the occurrence of the transfer reaction itself was essential and was proved (second year) both by in-situ XRD results from the ESRF and by XPS data from Sevilla. The evolution of the XPS spectra in $\text{MgH}_2 + \text{FeF}_3$ powders of INPG obtained in Sevilla showed disappearance of the $\text{Fe}2\text{P}_{1/2}$, $\text{Fe}2\text{P}_{3/2}$ and $\text{F}1s$ peaks from FeF_3 and appearance of the $\text{F}1s$ peak from MgF_2 and a weak $\text{Fe}2\text{P}_{3/2}$ peak from emerging Fe particles. Fluorine transfer reaction of the type of Eq. (1) forms protective intergranular MgF_2 and a fine nanoparticle dispersion of Fe in the Mg or MgH_2 powder.

The synchrotron XRD patterns of the as-milled composite indicated presence of the following phases: tetragonal β - MgH_2 , MgO, FeF_3 , Fe and Mg (next figure right side). The appearance of Fe from the start again indicated that some degree of transfer of F from FeF_3 to MgF_2 occurred during

the milling. An increase in the intensity of the Fe peaks and a decrease in the intensity of the FeF_3 peak were observed in the synchrotron XRD pattern at higher temperatures. This indicated that the fluorine transfer reaction is then completed during the first heating. Initially, presence of MgF_2 could not be clearly detected by XRD due to its low volume and electron density but XRD peaks of MgF_2 appeared after milling with large quantities of FeF_3 in the initial mixture.

Comparison of sorption kinetics of the Hydro-Quebec and the GKSS type powders with those of $\text{MgH}_2+\text{FeF}_3$ were previously performed and reported using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Subsequent to the Year 1 report, Sievert charge-discharge cycles were performed on mechanically milled nanocomposites of $\text{MgH}_2+2\%\text{Nb}_2\text{O}_5$ and $\text{MgH}_2+3\%\text{FeF}_3$.

The DSC curves in the Year 1 report and the Midterm report clearly showed that when MgH_2 is milled together with a few % transition metal fluoride (FeF_3), the sorption temperature is lowered by 50 C or more compared to MgH_2 milled with addition of the transition metal itself as in the Hydro-Québec invention or with transition metal oxide (Nb_2O_5). The Network subsequently compared desorption kinetics of MgH_2 nanocrystalline powders containing FeF_3 and Nb_2O_5 prepared at the INPG and tested during cyclic charge-discharge at the GKSS at 300C as shown in the next figures.



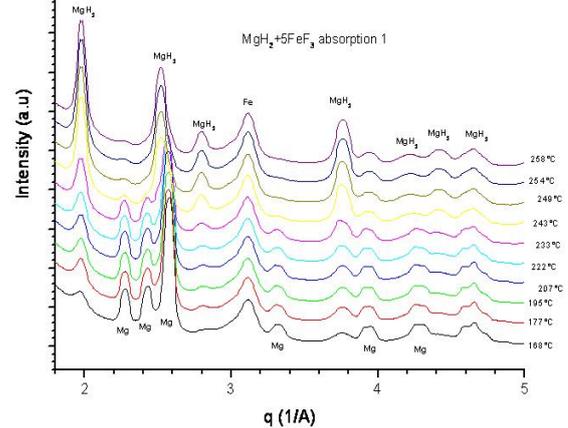
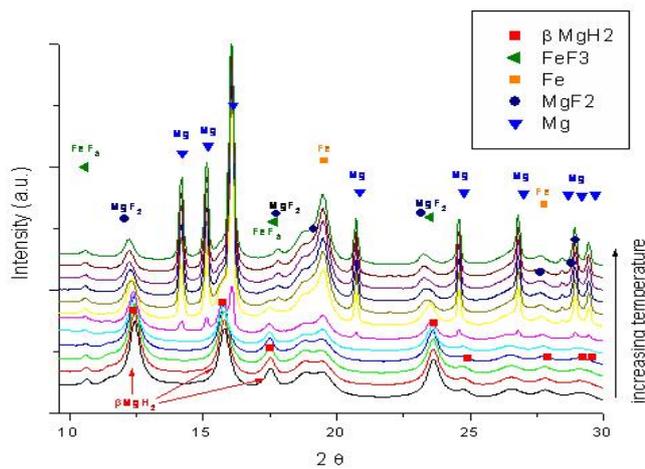
The H-sorption kinetics are clearly seen to be twice as fast as in the powders containing Nb_2O_5 . FeF_3 -containing MgH_2 powder thus appeared to be capable of one of the fastest H-sorption kinetics known to date in MgH_2 -based powders at 300°C (in 200 seconds) and improves with cycling.

An apparatus was conceived and built for gas-phase charge-discharge experiment in the beam at the ESRF and ILL partner. The apparatus was then used to test specimens from GKSS and INPG by several YRs (M. Venstrom-ESRF, S. Deledda-INPG, A. Borisova-INPG, N. Lupu-ILL) at the ILL neutron beam line D16 using deuterium instead of hydrogen to avoid incoherent scattering as observed in the Year 1 experiment with H_2 . The apparatus design and some results were presented in the Year 2 report including small angle scattering (SANS).

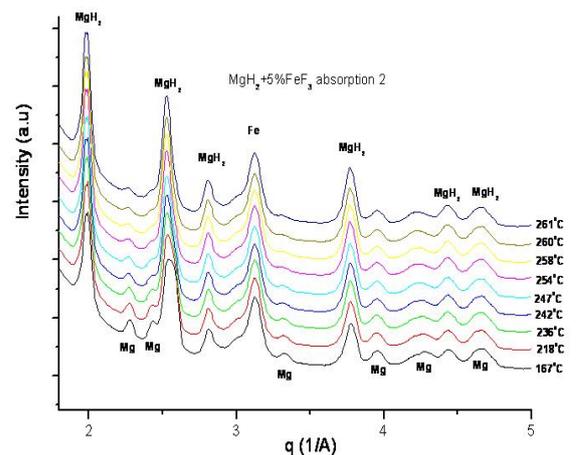
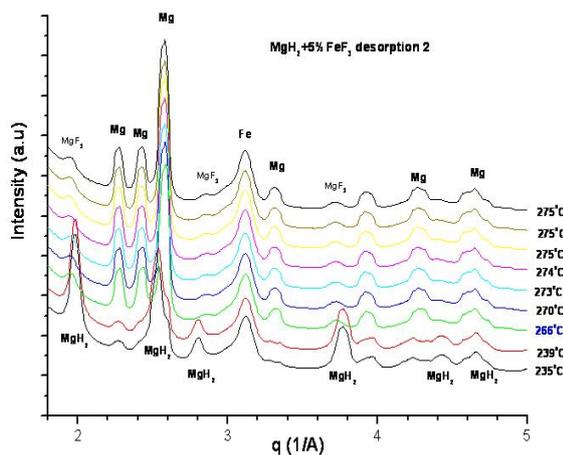
Subsequently, an improved version of the in-the-beam gas charge-discharge apparatus was extensively used on the ID11 beamline at the ESRF. Sorption kinetics in a number of new MgH_2 milled nanocomposites containing the following new catalysts in nanoparticle distributions were examined. These included FeF_3 , NiNb , FeTi and $\text{Nb}+\text{MgF}_2$.

Here we present some of the latest as yet unpublished results.

Initial desorption kinetics of $\text{MgH}_2+\text{FeF}_3$ are complicated by the completion of the F-transfer from Fe to Mg as in reaction (1) above. The details of this process can be seen in the next figure on the left. The Fe peak becomes more pronounced in the same temperature range as Mg peaks appear and thus in the 1st desorption, the F-transfer reaction and the H-desorption signals are coupled and next cycle measurements are indispensable (confirming the importance of the apparatus for in-situ charging). The subsequent absorption reactions are shown in the next figure on the right.



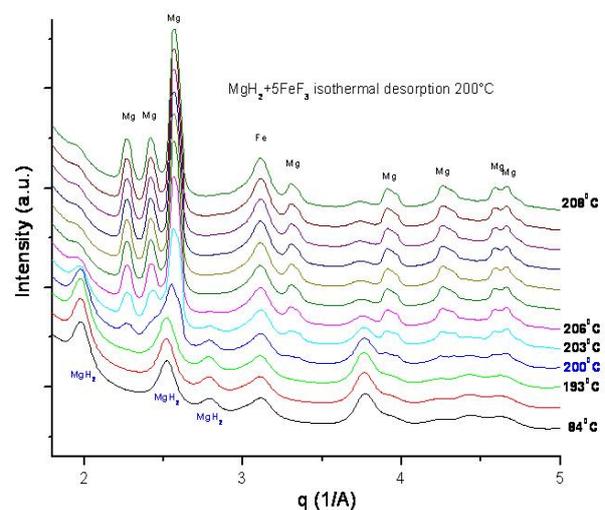
The Fe Bragg peak is now seen to be there from the start and remains unchanged but absorption kinetics appear to be fast near 230 C and the process is completed as the specimen is heated prior to reaching 260 C which is a remarkable result (heating rate is about 20 K per minute and spectra are taken every 10 seconds). The next two figures show the 2nd in-the-beam H-desorption and the 2nd H-absorption in the same nanocomposite powder.



It can be seen that desorption is completed around 260 C (left) and most interestingly, the 2nd absorption (right) appears to be nearly completed before acquisition begins at 167 C.

In view of this remarkable finding, a further isothermal H-desorption experiment was performed at 200 C and the figure on the right present the results.

It is clearly seen that when 5% FeF₃ is milled into nano-MgH₂ and after the F-transfer reaction is completed, the nanocomposite fully desorbs the hydrogen at much lower temperatures than previously reported and in particular at 200 C. This result which apriori appears inconsistent with thermodynamics of phase diagrams and the MgH₂ pressure-temperature-composition will be further discussed in our conclusions

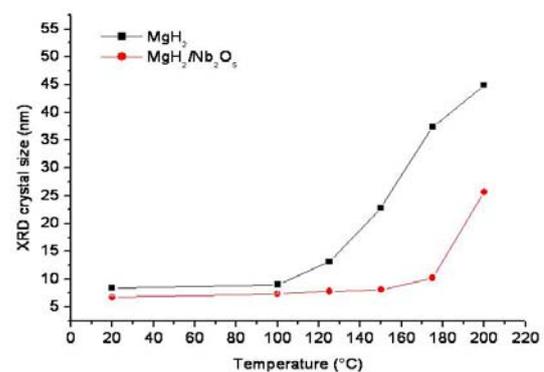


Before further discussing these recent highlights on catalytic H-sorption effects in Mg, it should be pointed out that the Network research has revealed that “composition” or “additive” effects are not the only major contributors to the kinetics of H-sorption and the details of the nanostructures as well as the powder and reactor materials’ mechanical properties that govern nanostructure formation during ball milling are crucial.

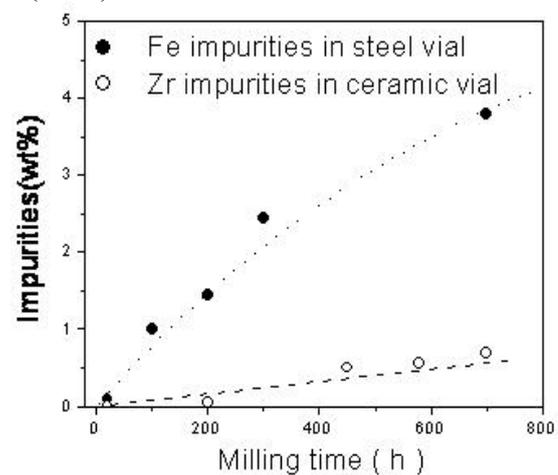
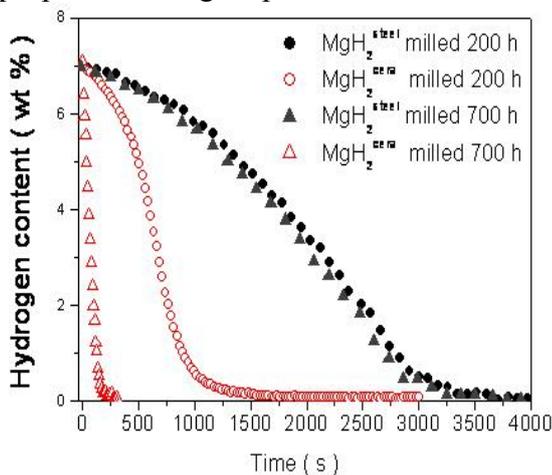
For example, in the course of investigation of hydrogen charging/discharging kinetics, the UAB and Uni-Sofia partners working on specimens supplied by the GKSS discovered that the hardness of the additives plays an important role in the particle size as revealed by the XRD measurements. These samples were prepared by milling MgH_2 with different additives for always the same time (120h). Other results came to indicate that particle size (as opposed to crystallite or coherent domain size) and specific surface (as opposed to specific internal interface) are key parameters and play major roles in the sorption/desorption kinetics in MgH_2 nanostructures.

In addition to their catalytic effect, it was found that added particles may play a role in maintaining the fine scale of the nanostructure.

For example, ICMS-Sevilla found that Nb_2O_5 nanoparticle catalysts actually reduce Mg grain growth during heating cycles (see figure on right) as is known in oxide-dispersion hardened steels where oxide particles pin the metal grain boundaries thus avoiding the coarsening of the structure.



The nature and mechanical properties of the vials and balls used for powder preparation were also found to play major roles. For example, in the two figures below, the work at GKSS compares properties of MgH_2 powders milled in steel and ceramic (ZrO_2) vials.



On the left we can see that sorption kinetics (at 300 C) are faster for MgH_2 milled in ceramic as compared to steel vials and continue to improve with further milling. On the right we see that ceramic mills also contaminate the powder less by their fragments due to their higher mechanical hardness which also results in a finer nanostructure of the milled powder (BET measurements yielded specific surfaces of 4 and 9 square-meters per gram after milling in steel and ceramic vials respectively).

The Network has thus succeeded in further improving sorption kinetics of H in Mg by manipulation of the (nano) structure and addition of catalytic particles. However the physical-chemical phenomena that contribute are numerous and complex and the progress achieved was only possible

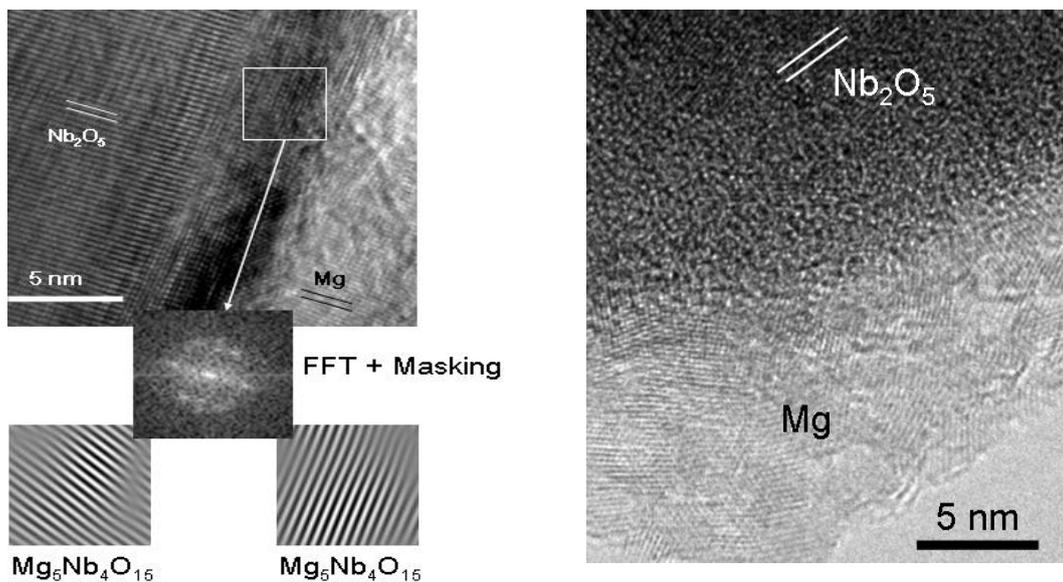
in the Network's multi-disciplinary and multi-team environment, including contributions from associated teams from outside the Network contract (M. Baricco of Torino and S. Enzo of Sassari). While specific surface per volume, specific interface per volume and metallurgical phenomena stabilizing nanostructures were found to play major roles as mentioned, the catalytic effect of nanoparticle additions to Mg/MgH₂ in H-sorption kinetics was confirmed and improved. It is said by the Network's industrial contacts that massive use of Mg in hydrogen storage and transport can be economical only if sorption "kinetics" are rapid at 180 C and below. For some catalysts, the Network has succeeded in reducing this temperature from 300 C to around 200 C without significant "thermodynamics" loss of capacity. The fastest kinetics have been achieved for nanostructured Mg/MgH₂ with additions of Nb₂O₅, and FeF₃. Empirically, what jumps to the eye is that Nb, Ti and Fe are all immiscible in Mg, a factor that is required for maintaining the integrity of the nanoparticle catalysts during temperature cycles. Beyond experimental empiricism, what can be said about the underlying atomistic phenomena common in the role of these very different catalysts?

For grain sizes of the scale attained by extensive ball-milling (10-30 nm), approximately 20% of the atoms of the nanoparticles are on the external interfaces and if the first layer under the interface is included, this fraction of atoms comes to nearly 40% of their total volumes. For the sake of discussion, consider an Fe/Mg interface. The interfacial energy σ , neglecting curvature effects, consists of a structural and a chemical component as in the zero-layer model [R. Becker, Ann. Phys., Paris 1938]:

$$\sigma = \sigma^{\text{str}} + \sigma^{\text{chem}} \approx (x_{\text{Fe}} \cdot \sigma_{\text{Fe}}^{\text{str}} + x_{\text{Mg}} \cdot \sigma_{\text{Mg}}^{\text{str}}) + m\Omega/A_m \quad (2)$$

where x_{Fe} and x_{Mg} are the component atomic fractions of the interface area, m is a geometric factor of the order of 0.25 and $\Omega = \Delta H_{\text{mix}}/x_{\text{Fe}} \cdot x_{\text{Mg}}$ is the molar exchange energy as in the regular solution model for molar heat of mixing ΔH_{mix} . The structural component σ^{str} is essentially due to topological disorder and atom-density deficit at the interface and is always positive while the chemical component σ^{chem} which accounts for hetero-atomic interactions at the contact surface is usually negative as alloying elements have negative heats of mixing ΔH_{mix} and results in a reduction of the total interfacial energy below σ^{str} . However, in immiscible systems such as Mg-Fe where hetero-atomic interactions are repulsive, $\Delta H_{\text{mix}} \gg 0$ and $\sigma^{\text{chem}} \sim m\Omega/A_m \gg 0$ contributes to significantly increase the interfacial energy σ at the Fe/Mg interfaces. On the other hand, Mg-H (and Fe-H) atomic interactions are attractive. It can therefore be safely predicted that hydrogen is attracted to the Mg/Fe interfaces in order to reduce the positive σ^{chem} component and the total interfacial energy σ . This idea is supported by the reported formation of metastable Mg₂FeH₆ [Huot et al, *J. Alloys Compounds*, 1998].

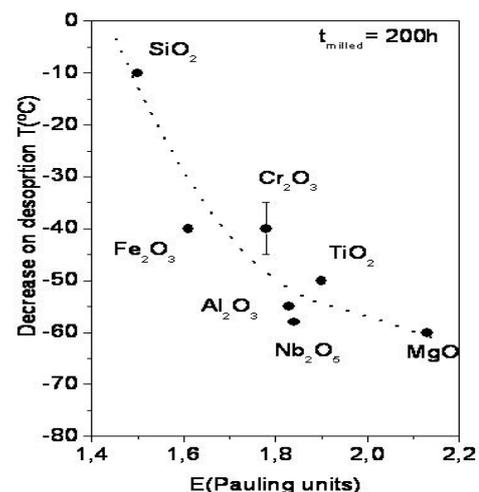
Thus without modifying the alloy composition (since Fe is immiscible in Mg), there is in fact an interfacial thermodynamic aspect to this "kinetic" acceleration of H-sorption. Since like all interfaces, Fe/MgH₂ nano-interfaces can act as fast diffusion paths or diffusion short circuits, the combination of the thermodynamic attraction of hydrogen to these interfaces and the fast diffusion kinetics along such interfaces explain the acceleration of hydrogen sorption kinetics in fine-grain Mg and MgH₂ with such particle additions.



As can be seen in the above HRTEM images, mixed oxides are formed at these interfaces for the larger Nb₂O₅ particles (for the very small particles, Nb appears to be fully reduced to act as a metal catalyst like Fe). The interfacial oxide layer appears to be amorphous.

Last but not least on this subject, a correlation has been discovered by the GKSS partner between the potency of an oxide catalyst and the nature of the metal-oxide bonding as presented in the next figure.

OXIDE	BOND(M-O)	ΔE (Pauling units)
MgO	Mg-O	2.13
TiO ₂	Ti-O	1.9
Nb ₂ O ₅	Nb-O	1.84
Al ₂ O ₃	Al-O	1.83
V ₂ O ₅	V-O	1.81
Cr ₂ O ₃	Cr-O	1.78
Fe ₂ O ₃	Fe-O	1.61
CuO	Cu-O	1.54
SiO ₂	Si-O	1.5



This correlation may bring further fundamental input but in view of other Network findings implicating the mechanical properties of the additives on the morphology (scale of nanostructure), work is needed to further establish the contributions of the “chemical” and “mechanical” role of the oxide catalysts.

Electrochemical hydrogen insertion and cycling:

The activity performed by the Electrochemical Task Force IV has 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 MgH₂+Nb₂O₅-catalyst electrodes at various compaction pressures was studied in Dortmund as found in our previous reports. It was found that that compaction with PTFE + C significantly increases H-insertion capacity. 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, Nb₂O₅-MgH₂ Hydride prepared by GKSS was shaped into thin film electrodes. 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.

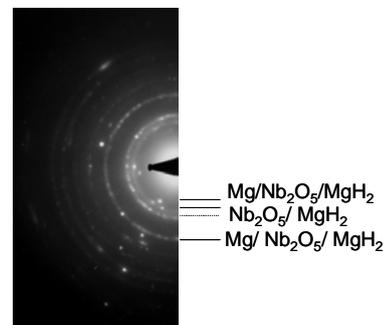
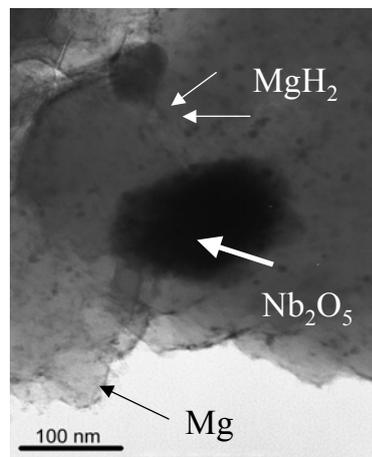
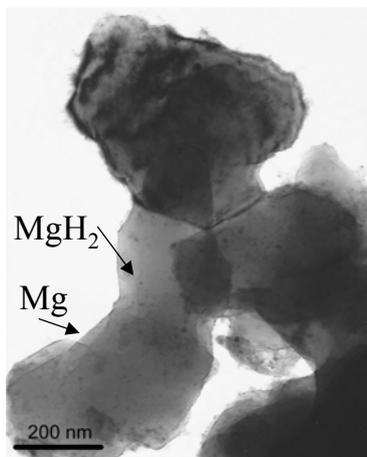
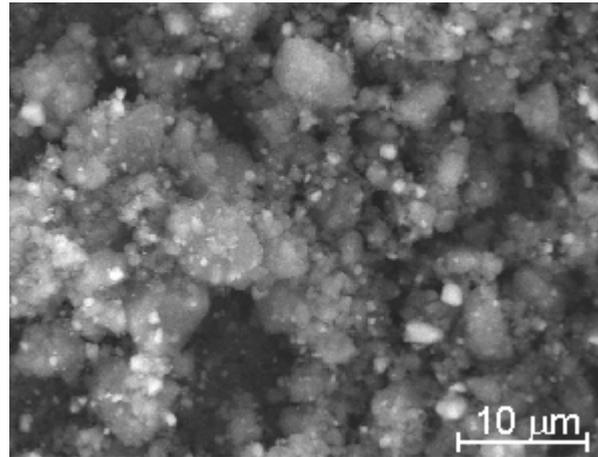
However, the best results were obtained with MgH₂ composites containing initially FeF₃ nanoparticles. With the fluoride, the storage capacity is preserved during cycling and furthermore increases linearly from 85 mAh.g⁻¹ at the first cycle to 1600 after several cycles.

Unfortunately, the voltammograms of all the studied samples recorded at 25°C with the same potential scan rate exhibited 2 peaks at -0.3V and -0.6V in charge and -0.4V and -0.08V in discharge. 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.

The comparison of the electrochemical isotherms of pure MgH₂ and MgH₂ 5%*m*FeF₃ showed the influence of the grain size and of FeF₃ catalysts on the electrode potential. When the grain size decreases, the potential of pure MgH₂ electrode increases during discharge and decreases during charge. The reverse variation is observed on the isotherms of the doped electrode: the discharge potential plateau is decreased with decreasing grain size and the charge potential is increased with grain size. This difference between the electrochemical isotherms of pure and doped electrodes illustrates the role of catalysts: it modifies significantly the surface tension and decreases the hysteresis between the two parts of the isotherm. Nevertheless, questions remain: what is the effect of some 1% percentage of ceramics pollution generated during the 1000h milling in the ceramic vials? What is the influence of the Mg(OH)₂ layer on the interface resistance of the electrode? In any case, the recovered capacity increases when the grain size decreases.

The influence of Nb₂O₅ catalysts on the performance of nanocrystalline Mg powder as an electrode material for electrochemical hydrogen charging processes in a 6M KOH electrolyte at room temperature was studied in detail by the UNI-Dortmund partner team. The powder was prepared by the GKSS-group, in different batches and by different operators.

Microstructural investigations by SEM (next fig.a) and TEM (next fig. b-d) of desorbed MgH₂ powders without and with 2 mol% Nb₂O₅ powder showed a Mg particle size of 5-10 μm and inhomogeneously distributed catalyst. X-ray as well as electron diffraction of MgH₂ without and with catalyst after thermal desorption at 300°C (next Fig. c) revealed the precipitation of nanocrystalline MgH₂ within the Mg particles. The observed hydrogen content after thermal desorption was 0.15 wt.% H₂; this explains the existence of nanocrystalline MgH₂ particles as seen by TEM. The grain size of the Nb₂O₅ catalyst of Mg / Nb₂O₅ powder was found to be 50-200 nm.

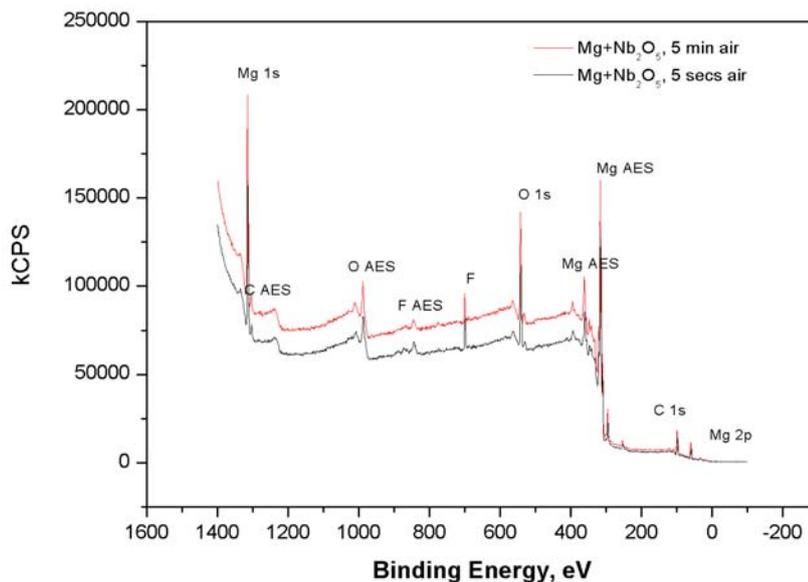


b) (a) SEM and (b) - (d) TEM of desorbed MgH_2 powders without and with 2 mol% inhomogeneously distributed Nb_2O_5 .

Investigations of Mg powder without and with 2 mol% Nb_2O_5 as electrode material for electrochemical hydrogen charging revealed that compaction of this powder provides good mechanical stability and good conductivity to allow the dissociation and adsorption of hydrogen at the surface as well as diffusion into the material. XPS measurements (Sevilla, see next fig.) of compressed electrodes (6.2 N/mm^2) revealed no significant difference in the oxidation behavior and oxide layer thickness in air after 5 s and 5 min exposure time which is relevant for operating the electrochemical measurements.

During hydrogen charging of Mg and $\text{Mg/Nb}_2\text{O}_5$ electrodes strong influences of (1) compaction parameters, (2) the current density on the hydrogenation behavior and (3) the catalyst on the hydrogenation were observed.

A strong influence of the catalyst was observed with decreasing current densities for the upper hydrogen charging limit. While the storage capacity of about 0.4 wt.% H_2 of the Mg-electrode changes only by a small amount to lower hydrogen contents of 0.35 wt.% with decreasing current density and a charging time of 30 min, the storage capacity as well as the kinetic of $\text{Mg/Nb}_2\text{O}_5$ electrodes increased significantly up to 1 wt.% H_2 at a charging time of 30 min with decreasing current density.



XPS measurements of compressed Mg / Nb₂O₅ / C / PTFE electrodes (6.2 N/mm²) after oxidation for 5 s and 5 min in air (measured during the visit of the YR in Seville, Spain).

Electrochemical properties of ball milled Mg–La(Mm)Ni₅ nanocomposites: in a series of Mg–x at% Mm(La)Ni₅ (Mm–La, Ce–rich mischmetal) nanocomposites were investigated in galvanostatic conditions in Sofia. For all the compositions, except Mg – 5at% MmNi₅, during the first 1– 2 hours of milling under argon, MgH₂ decomposed completely and during the following milling, formation of new intermetallic compounds took place (e.g. Mg₂Ni). Significant differences in the electrochemical properties, expressed in electrochemical charge/discharge curves were found between the composites with LaNi₅ and these with MmNi₅ as well as between the composites with different MmNi₅ content. For all the compositions studied relatively low discharge capacities were obtained.

Joint Publications**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

T. Spassov (Sofia), ***Pau Solsona*** (Sofia-UAB), S. Bliznakov (Sofia), S.Surinach (UAB), M.D.Baró (UAB), “Synthesis and hydrogen sorption properties of nanocrystalline $Mg_{1.9}M_{0.1}Ni$ ($M=Ti,Zr,V$) obtained by mechanical alloying” *Journal of Alloys and Compounds* 356-357 (2003) 639-643.

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