	Experiment title: Role of Catalytic Particles in H-sorption Kinetics in Mg Nanocomposites	Experiment number: ME-438
Beamline: ID11	Date of experiment: from: 2002/II to:2004/II	Date of report: 18/08/04
Shifts: 48	Local contact(s): Dr Gavin Vaughan	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

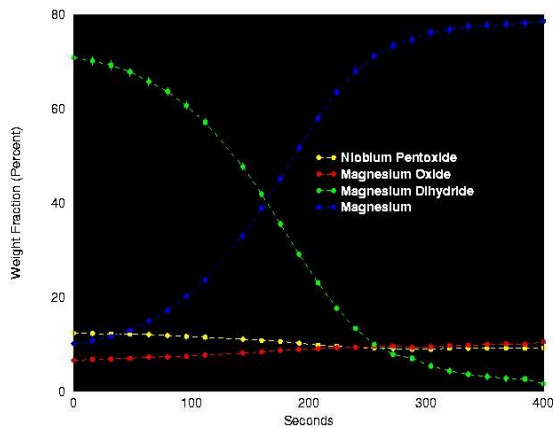
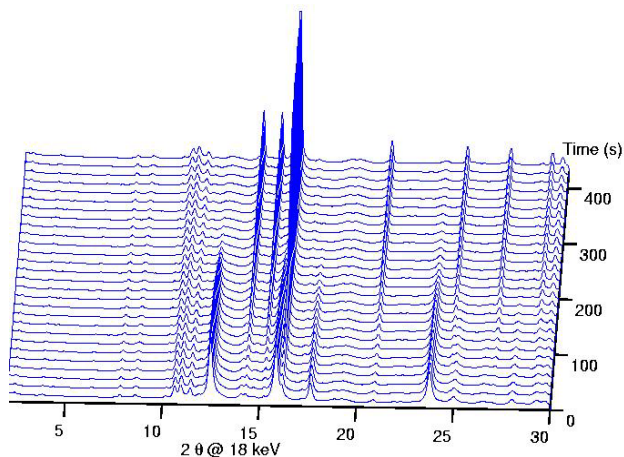
Directeur* Alain Reza Yavari, CNRS-Institut National Polytechnique de Grenoble, France
 Professor Maria Dolores Baro*, Universitat Autònoma de Barcelona, Spain
 Professor Rudiger Bormann, GKSS Forschungszentrum Geesthacht, Germany
 Professor Asuncion Fernandez*, CSIC-ICMSE, Sevilla, Spain
 Dr Giovanna Fragneto*, Institut Laue-Langevin (ILL), France
 Professor Uwe Köster, University of Dortmund, Germany
 Dr (Reader) John Sykes, University of Oxford, UK

Report:

ME-438 was submitted by the main participating teams of the EU RTN Network project HPRN-CT-2002-00208 entitled: *“Improved Hydrogen Sorption Kinetics in New Magnesium Composites for Clean Energy Storage and Transport”* coordinated by the main proposer (ARY). The EU Network runs from 10/2002 to 10/2005, includes the ESRF Materials Science group (Å. Kvik and G. Vaughan) and financed the recruitment of postdoc Dr Marie Vennstrom at the ESRF for 12 months (07/03 to 07/04). For further information on this network please see <<http://www.inpg.fr/RTN-MgH2>>.

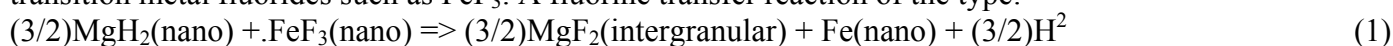
The ESRF experiments concerned nanostructured powders of Mg and MgH₂ doped with a few % nanoparticle catalysts for acceleration of H-sorption. Metal hydrides offer a safe medium for transmission and storage of hydrogen energy and Mg can pick up 7.6 w% of H₂ and its cost is low. However it requires temperatures T > 400°C for desorption. In Mg with nanometer grain size, which can be inexpensively prepared by mechanical milling, H₂ sorption kinetics are faster but hydrogen desorption kinetics (about 30 minutes or more even at 300 C) remains too slow while most large-scale applications require operating temperatures less than or near 200 C. Recently, it has been shown by the partners of our EU Network and others that introduction of nanoparticles of mixed valence transition metals such as Nb, V, Fe, Cr, Ni, Ti improves sorption kinetics of H₂ in Mg. The mixed valence transition metal nanoparticles are immiscible in magnesium and the transition metal-Mg interfaces are thought to act as catalysts to accelerate H-sorption kinetics and in particular in the breaking of H₂ molecules into adsorbed protons.

Introduction of about 1 mole% of nanoparticles of mixed valence transition metal oxides such as Nb₂O₅, Cr₂O₃, V₂O₅, Fe₃O₄, Mn₂O₃ also improves sorption kinetics of H₂ in Mg. Since the magnesium oxide MgO is more stable than these oxides, it is likely that interaction with Mg will reduce the transition metal oxides during temperature cycling and generate a dispersion of transition metals within the magnesium matrix. We have therefore undertaken to determine if the oxide particles play a specific catalytic role or if their reduction through MgO formation amounts to an alternative manner of introducing the transition metal nanoparticles. The next two figures present typical XRD results obtained at the ESRF on MgH₂+ 2% Nb₂O₅ nanopowders during in-situ heating and the desorption reaction (MgH₂ => Mg + H₂). A decrease in the amount of Nb₂O₅ and an increase of MgO during the desorption is detected from the Bragg peak intensities. Since the oxygen for MgO formation comes from the reduction of Nb₂O₅, it should lead to formation of Nb metal and/or a mixed or less oxygen rich Nb oxide traces. This has in fact been documented by HRTEM at partner institutes.

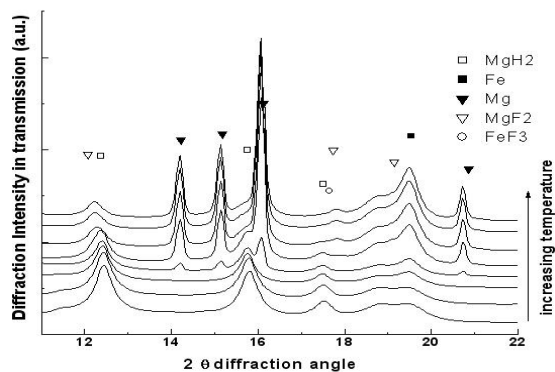
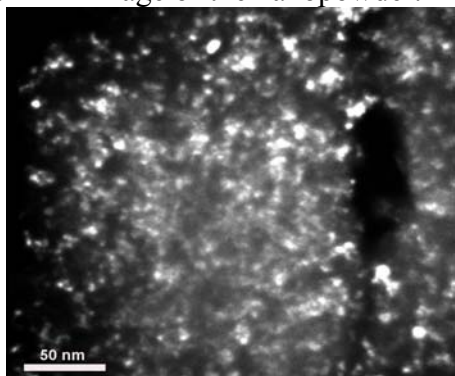


It was found in Japan that a reaction between hydrides and F^- ions in aqueous solution forms a protective fluoride layer which is permeable to hydrogen, replacing the surface oxide layer.

One objective of the present research was to combine the beneficial effect of fluorinated interfaces with the catalytic effect of transition metal nanoparticles. We have achieved this by the addition of a few mole % transition metal fluorides such as FeF_3 . A fluorine transfer reaction of the type:



then generates pure Fe nanoparticles within the Mg or MgH_2 matrix and protective MgF_2 at interfaces as can be seen in the in situ XRD patterns obtained at the ESRF presented in the next figure together with a dark field TEM image of the nanopowder.



The occurrence of chemical reaction (1) documented at the ESRF by XRD has been confirmed by magnetisation measurements and XPS. The Fe nanoparticles generated by our chemical reaction then act as catalysts to accelerate the kinetics of hydrogen sorption to the fastest known recorded date in MgH_2 -based powders. The reaction also lowers the H-sorption temperatures by a further 50 C which is a critical step towards the development of a new family of application-enabled Mg-based.

In the course of this work Dr G. Vaughan and Dr M. Vennstrom (EU postdoc on the project) succeeded to build a simple but efficient setup for in the beam H-charge/discharge cycles on small (50 mg) hydride powders. This setup is being used for the last beam time allocation of this long-term project.

Joint Publications with ESRF scientists of this project:

1) "Structural evolution and metastable phase detection in MgH_2 -5%NbH nanocomposite during in-situ H-desorption in a synchrotron beam", A.R. Yavari, J.F.R. de Castro, G. Vaughan, G. Heunen *Journal of Alloys and Compounds*, **353** (2003) 246-251.

2) "Transition metal and transition metal fluorides as catalysts in MgH_2 -based nanocomposites"

W.J.Botta F., J.F.R. de Castro, G. Vaughan and A.R. Yavari,

presented at ISMANAM 2004, Sendai Japan, to appear in the *J. Metastable & Nanocryst. Mater.*

3) "Chemical reaction with new nanoparticle catalysts brings temperatures for H-sorption in MgH_2 nanopowders close to major application threshold", A. R. Yavari, A. LeMoulec, O. Friedrichs, F. Ribeiro de Castro, S. Deledda, G. Vaughan, A. Fernandes, W. J. Botta, Å. Kvick and T. Klassen, Submitted to *Nature Materials* 2004.

Two other publications are in preparation.