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High-pressure techniques applied to the synthesis and characterization of light metal hydrides

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Introduction

The application of high hydrogen pressure techniques, such as high- pressure ball milling (HP-BM) and high-pressure differential scanning calorimetry (HP-DSC), is advantageous to synthesize novel hydrides for hydrogen storage under non-equilibrium conditions and to characterize their complex thermodynamic and kinetic properties. We have developed a novel synthesis technique [1], which involves high-energy ball milling in an especially designed vial, allowing *in-situ* monitoring of temperature and, more importantly, of hydrogen pressure in the pressure range of 1-150 bar. This technique has been proven useful in terms of promoting nanocrystallinity, hydride formation, monitoring and controlling decomposition reactions during milling as well as for direct synthesis. In the present study, two different classes of hydrides were investigated: (a) Mg and Mg-based alloys, (b) lithium alanate and modified lithium alanates.

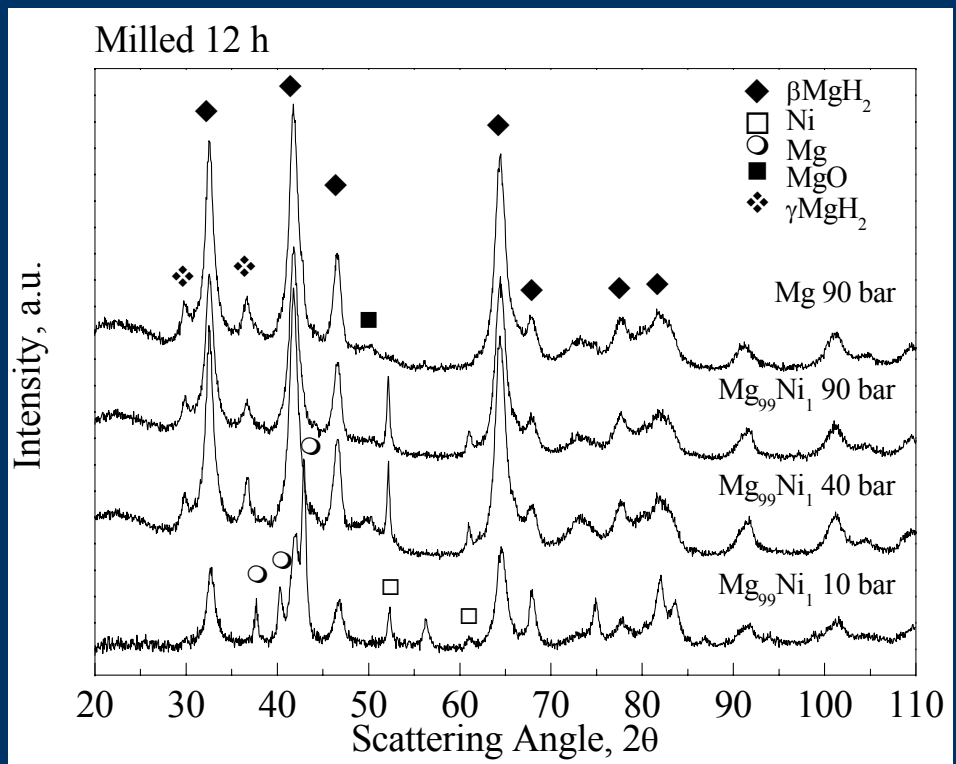
[1] presented at EMRS meeting 2nd June 05, Strasbourg, submitted to J. Alloys Comp.

Synthesis and characterization

- High energy ball milling under hydrogen or argon atmosphere (1-150 bar) with in-situ pressure and temperature monitoring
- High pressure differential scanning calorimetry (1-150 bar) working in a dynamic mode, placed in a glove box
- XRD (Rietveld refinement)
- Gravimetric analysis (1-20 bar)

Mg and $Mg_{99}Ni_1$

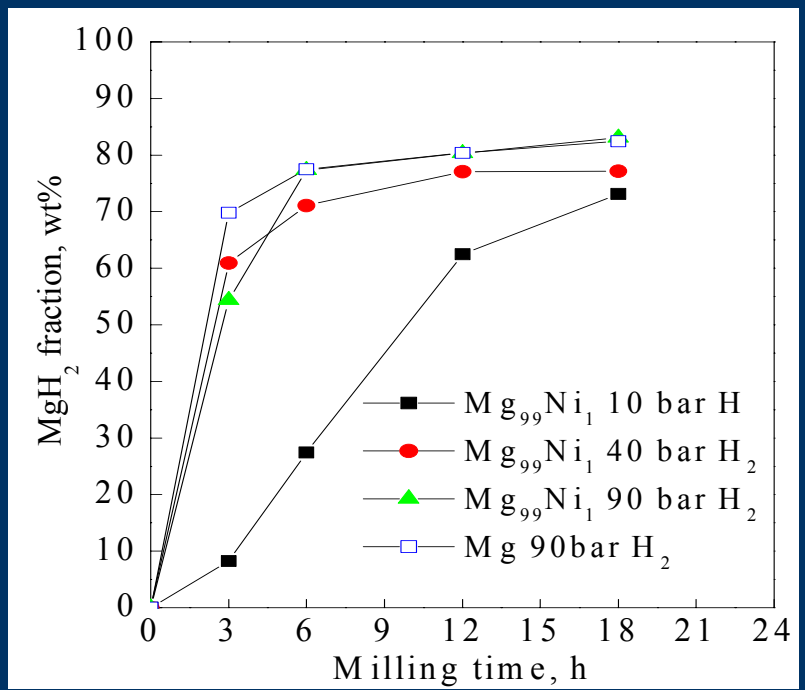
High-pressure ball milling (10, 40 and 90 bar)

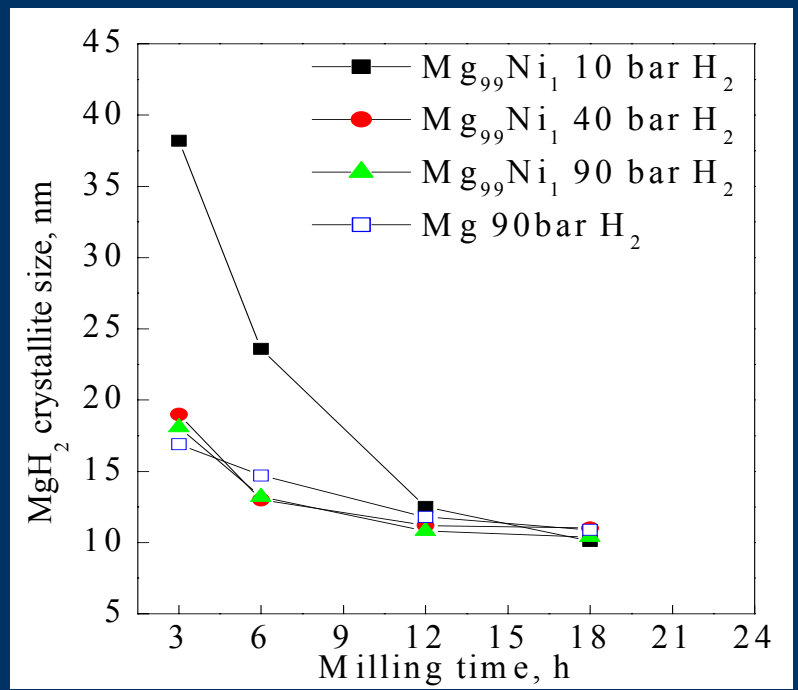


- The samples milled at 40 and 90 bar show complete conversion into the hydride after 12 h of milling
- A lower rate of hydrogenation was observed in the case of the sample milled under 10 bar H_2
- No formation of the metastable γ-MgH_2 was detected for the sample milled under 10 bar of hydrogen
- In all other cases the amount of γ-phase, evaluated from the Rietveld refinement, was between 10-15 wt.%

Mg and $Mg_{99}Ni_1$

Rietveld refinement





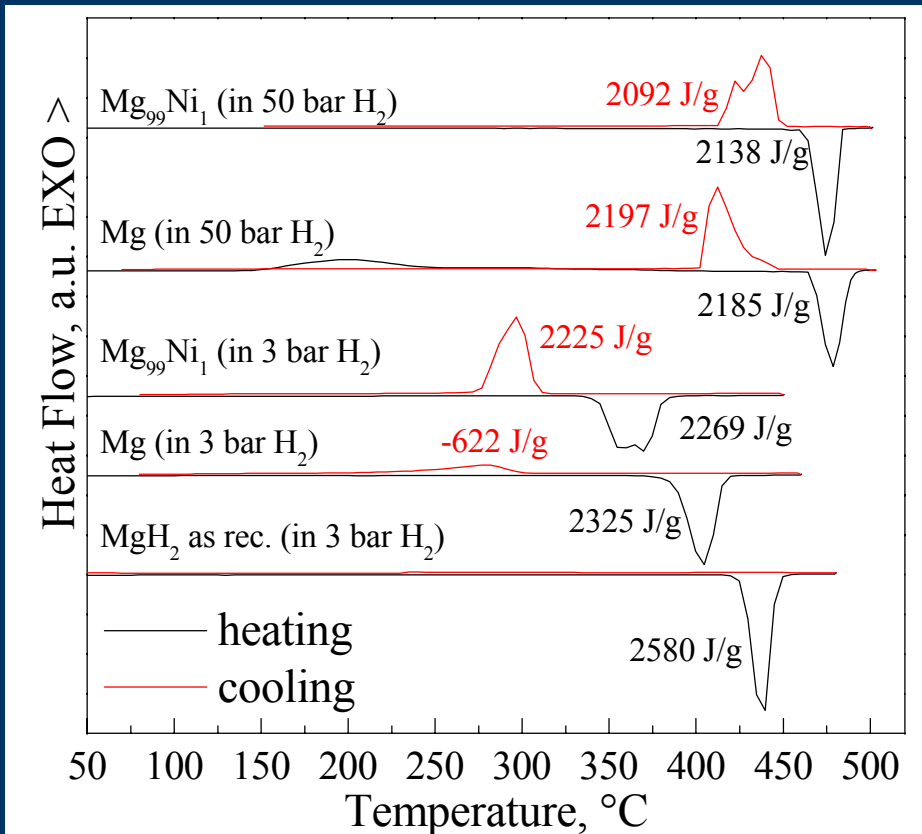
Strong influence of the hydrogen pressure on the conversion rate of Mg into β–hydride during milling

High hydrogen pressure promotes nanocrystallinity for very short milling times

Mg and $Mg_{99}Ni_1$

High-pressure DSC

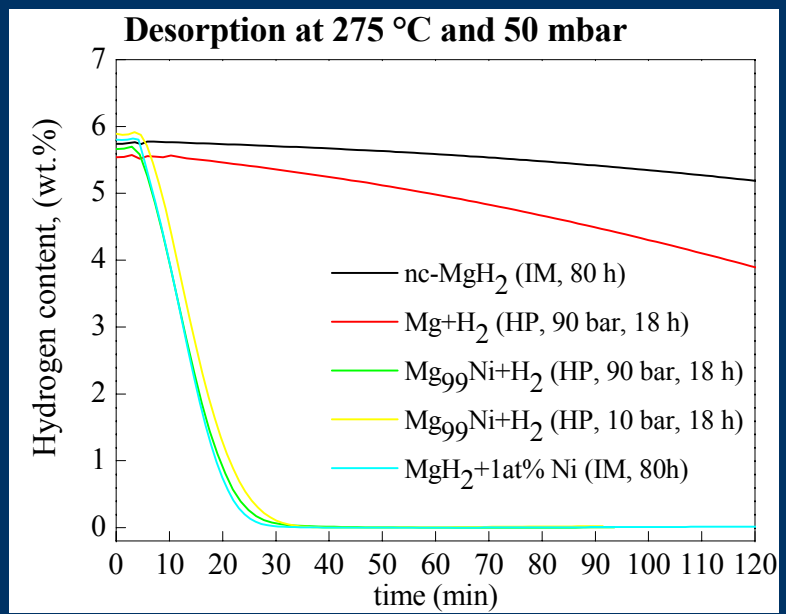
Mg and $Mg_{99}Ni_1$ milled under 90 bar of H_2
DSC performed at 3 and 50 bar respectively

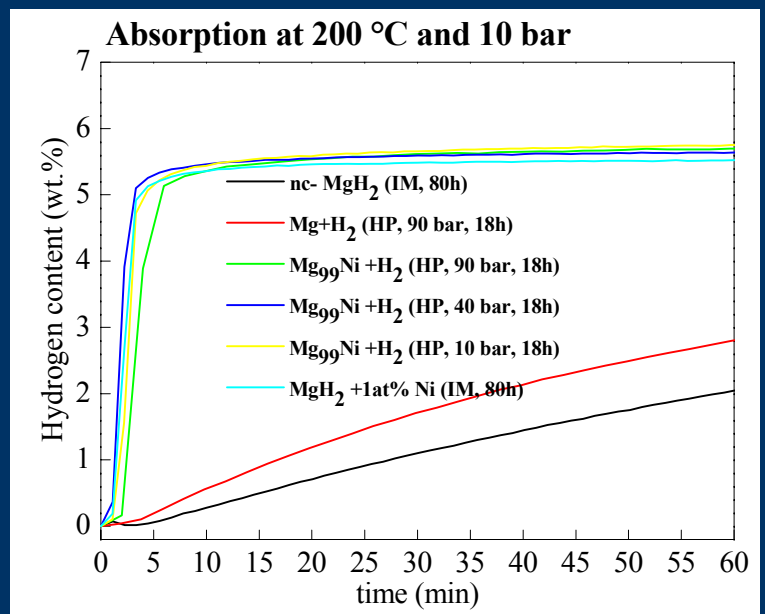


- **Increased hydrogen pressure shifts the desorption/absorption peaks to higher temperatures**
- **The re-absorption during cooling depends on the pressure applied**
- **and/or the catalytic effect of Ni**
- **The evaluated enthalpies are in agreement with the value obtained for micro-crystalline MgH_2 (as received)**

Mg and $Mg_{99}Ni_1$

Gravimetric analysis

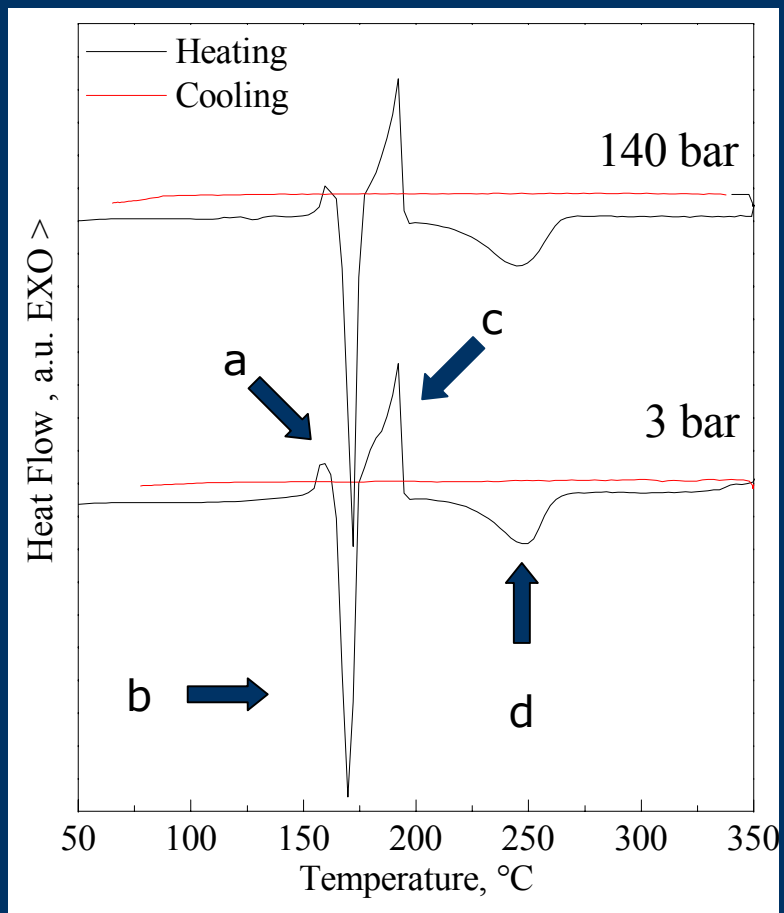




MgH_2 synthesized by high pressure milling (90 bar H_2) shows better kinetics than nanocrystalline MgH_2 obtained by milling 80 h under argon atmosphere

$LiAlH_4$ and $LiAlH_4$+10 mol%MgH_2+2 mol% $TiCl_3$

Thermal stability of $LiAlH_4$ under different hydrogen pressure



DSC measurements performed at different hydrogen pressures (3, 10, 50 and 140 bar) show, contrarily to what is observed in the case of Mg and Mg-based alloys, no significant shift of the decomposition peaks.

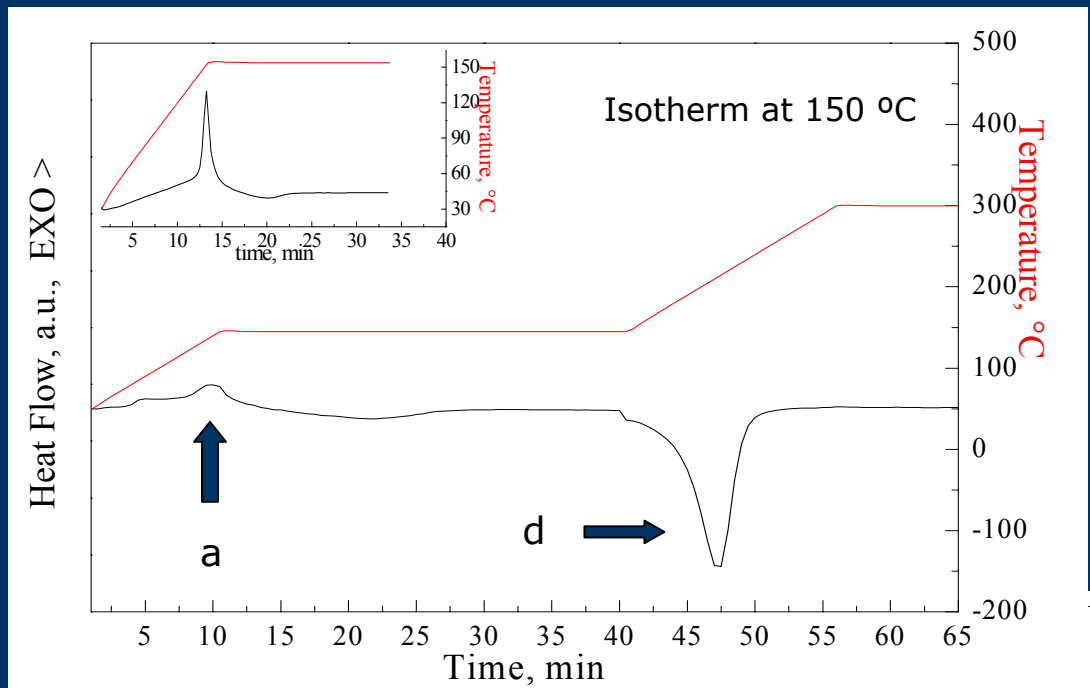
The decomposition is described by the following steps:

a) ~150°C start of solid state decomposition of $LiAlH_4$ into Li_3AlH_6

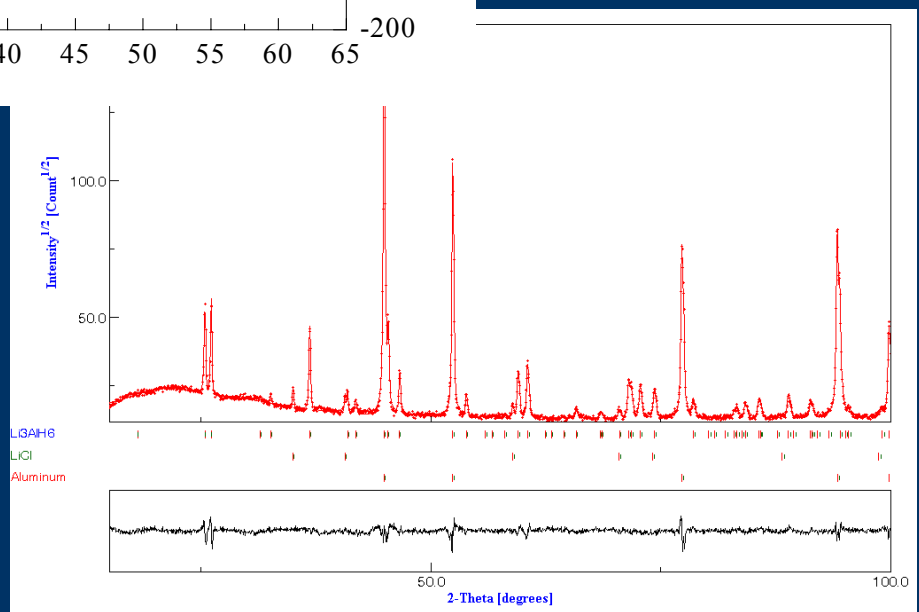
b) ~160°C melting of $LiAlH_4$

c) decomposition of liquid $LiAlH_4$ into Li_3AlH_6, Al and H_2

d) decomposition of Li_3AlH_6 into LiH, Al and H_2

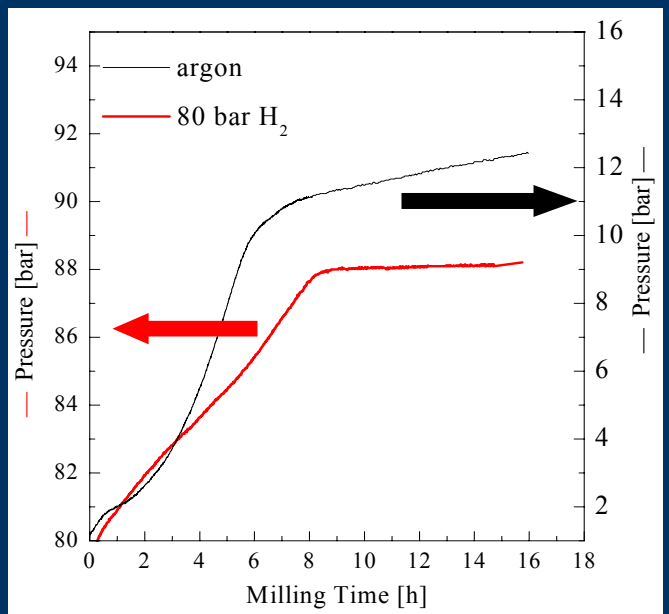


After the isothermal step at 150 °C, a complete solid state decomposition of $LiAlH_4$ into Li_3AlH_6 is observed by XRD

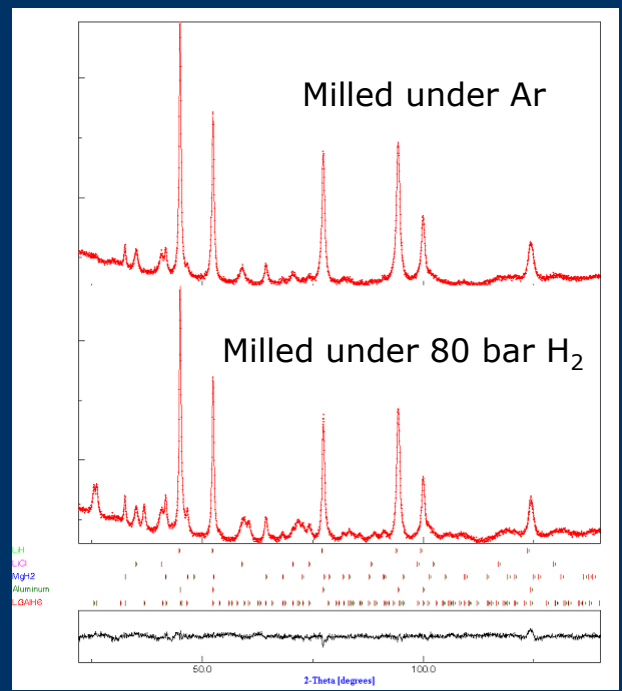


Decomposition of $LiAlH_4+MgH_2+TiCl_3$ during ball milling

in-situ **monitoring of decomposition during milling**



XRD after milling



- **The applied hydrogen pressure of 80 bar hinders the decomposition of the hydride during milling**
- **After 16 h of milling an increase of pressure of ~12 bar was observed in the case of the sample milled under argon while the sample milled under hydrogen shows an increase of 8 bar**
- **The sample milled under argon shows a complete decomposition into LiH, Al and H_2 after 16 h of milling while the pattern of the sample milled under hydrogen shows the presence of Li_3AlH_6**

Summary

- High-pressure techniques are a powerful tool for the synthesis and complete thermodynamic and kinetic characterization of light metal hydrides.
- Milling Mg at high hydrogen pressure allows to shorten the time for the complete conversion into the hydride (12 hours even without catalysts) with the formation of a very fine powder with crystallite size of the order of tens of nanometers during milling.
- It is possible to follow the decomposition of the $LiAlH_4$ during milling and, by selecting an adequate hydrogen pressure, to suppress it to some extent.
- Under suitable experimental conditions, solid state decomposition of $LiAlH_4$ into Li_3AlH_6 can be achieved and monitored by DSC.

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COOPERATIONS:

- University of Birmingham, UK
- University of Fribourg, Schweiz
- Johnson-Matthey, UK
- GKSS, Germany
- FZK, INT, Germany
- University of Padua, Italy

Experimental set-up

General Facilities:

Synthesis

- induction and arc melting, forming, powder metallurgical routes, melt spinning, mechanical alloying, heat treatment and coating of materials

Solid state analysis

- chemical analysis of the overall composition and of dope additives
- x-ray diffraction (also *in-situ* XRD at elevated temperatures and hydrogen pressures)
- analytical high resolution scanning and transmission electron microscopy and atomic force microscopy
- thermal analysis: differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA)
- surface analysis: XPS and Auger
- electrochemical characterisation, measurement of specific surface area (BET)

Specialised techniques:

- reactive milling technique (vibration ball milling: -196 – 300°C, 10 bar hydrogen; planetary milling: 150 bar with in-situ pressure monitoring)
- dedicated high pressure DSC (dynamic mode: <150 bar hydrogen, 500°C) in a glove box ensuring a reliable thermodynamic and kinetic characterisation of very reactive materials
- intelligent gravimetric analysis (Hiden IGA: <20bar, 500°C)
- pressure-composition-temperature-analysis (pcT: <200bar, 400°C)
- thermal desorption spectroscopy (TDS)
- hot extraction (Leco)