16th International Symposium on Metal-Hydrogen Systems
28 October – 2 November 2018, Guangzhou, China

MAGNESIUM BASED MATERIALS FOR HYDROGEN BASED ENERGY STORAGE: PAST, PRESENT AND FUTURE

Volodymyr Yartys

Institute for Energy Technology

NORWAY

November 1st, 2018

16 research units from Australia, China, Denmark, France, Germany, Japan, Italy, Israel, Netherlands, Norway, Russia, South Africa, Spain and United Kingdom

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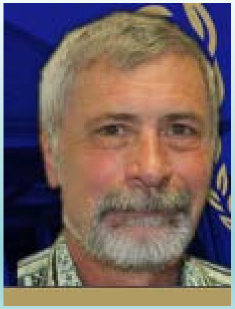
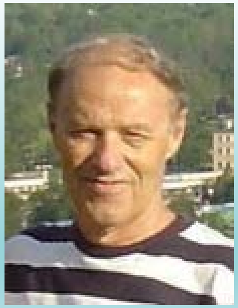
GENERAL PROPERTIES AND HYSTORICAL OVERVIEW

				
MICHAEL LOTOTSKYY	**JOSE R. ARES**	**COLIN JIM WEBB**	**TORBEN RENÉ JENSEN**	**VOLODYMYR YARTYS**

NEW INTERMETALLIC AND COMPEX HYDRIDES OF Mg

		
BJØRN HAUBACK	**ISAAC JACOB**	**VOLODYMYR YARTYS**

NANOMATERIALS

PETRA DE JONGH

LUCA PASQUINI

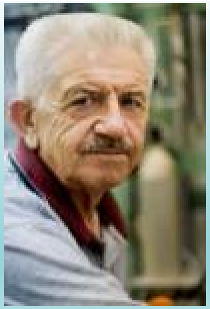
ETSUO AKIBA

KINETICS

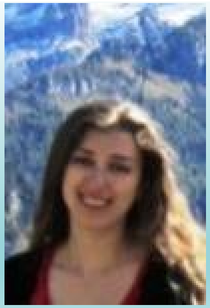
MARCELLO BARICCO

COMPOSITES WITH CARBON

EUGEN RABKIN



VLADIMIR M. SKRIPNYUK



LARISA POPILEVSKY

HEAT STORAGE


CRAIG BUCKLEY


MARK PASKEVICIUS


MICHAEL FELDERHOFF


TERRY HUMPHRIES

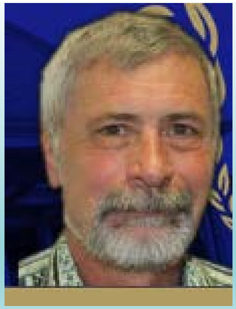

VERONICA SOFIANOS


RENE ALBERT

REACTIVE BALL MILLING


MICHEL LATROCHE

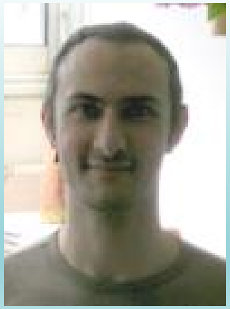
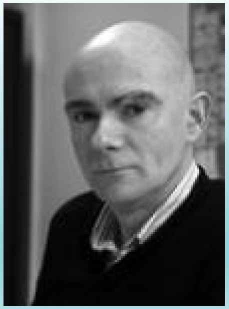
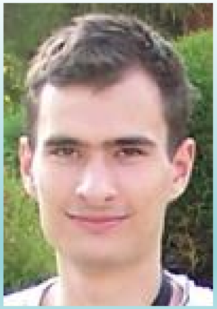

FERMIN CUEVAS


MICHAEL LOTOTSKYY


ROMAN DENYS


VOLODYMYR YARTYS

Mg-H SYSTEM AT HIGH PRESSURES: THEORETICAL AND EXPERIMENTAL STUDY

				
NATACHA BOURGEOIS	JEAL-CLAUDE CRIVELLO	JEAN MARC JOUBERT	VLADIMIR ANTONOV	MIKHAIL KUZOVNIKOV

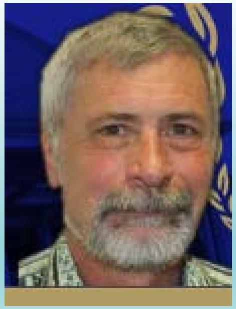
CATALYSIS

		
MIN ZHU	HUI WANG	COLIN JIM WEBB

HYDROGEN STORAGE SYSTEMS

JOSE BELLOSTA VON COLBE

MARTIN DORNHEIM



MICHAEL LOTOTSKYY

MAGNESIUM HYDRIDE AS A POWDER

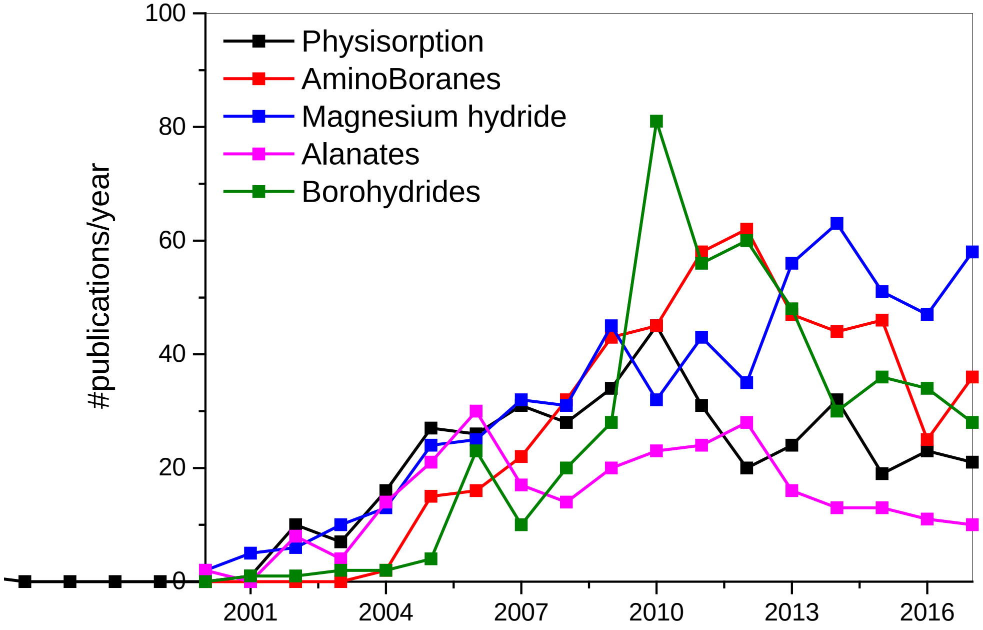
DAVID GRANT

GAVIN WALKER

ALASTAIR STUART

AMELIA MONTONE

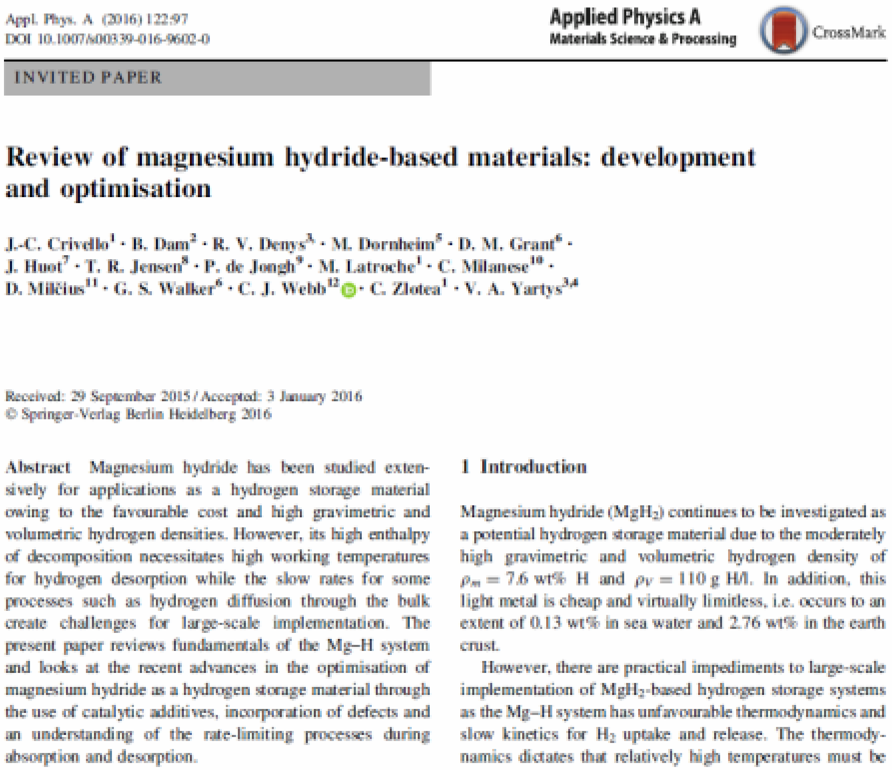
Number of articles published during the last years 2000-2017 having “hydrogen storage” and the “name” of the respective compound. Source: SCOPUS



GREAT INTEREST WORLDWIDE

(Magnesium+Hydride) most publications in 2000-2017

TWO EARLIER PUBLISHED REVIEWS BASED ON THE WORK OF IEA TASK32



Appl. Phys. A (2016) 122:97
DOI 10.1007/s00339-016-9602-0

Applied Physics A
Materials Science & Processing

INVITED PAPER

Review of magnesium hydride-based materials: development and optimisation

J.-C. Crivello[1] · B. Dam[2] · R. V. Denys[3] · M. Dornheim[5] · D. M. Grant[6] ·
J. Huot[7] · T. R. Jensen[8] · P. de Jongh[9] · M. Latroche[1] · C. Milanese[10] ·
D. Milčius[11] · G. S. Walker[6] · C. J. Webb[12] · C. Zlotea[1] · V. A. Yartys[3,4]

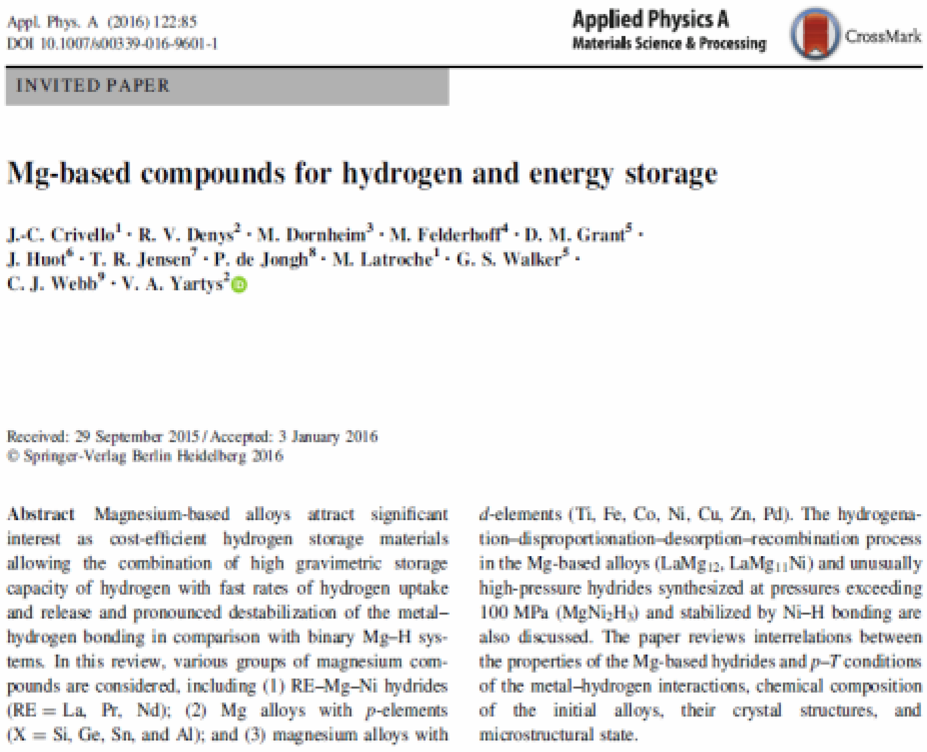
Received: 29 September 2015 / Accepted: 3 January 2016

Abstract Magnesium hydride has been studied extensively for applications as a hydrogen storage material owing to the favourable cost and high gravimetric and volumetric hydrogen densities. However, its high enthalpy of decomposition necessitates high working temperatures for hydrogen desorption while the slow rates for some processes such as hydrogen diffusion through the bulk create challenges for large-scale implementation. The present paper reviews fundamentals of the Mg–H system and looks at the recent advances in the optimisation of magnesium hydride as a hydrogen storage material through the use of catalytic additives, incorporation of defects and an understanding of the rate-limiting processes during absorption and desorption.

1 Introduction

Magnesium hydride (MgH_2) continues to be investigated as a potential hydrogen storage material due to the moderately high gravimetric and volumetric hydrogen density of $\rho_m = 7.6$ wt% H and $\rho_V = 110$ g H/l. In addition, this light metal is cheap and virtually limitless, i.e. occurs to an extent of 0.13 wt% in sea water and 2.76 wt% in the earth crust.

However, there are practical impediments to large-scale implementation of MgH_2-based hydrogen storage systems as the Mg–H system has unfavourable thermodynamics and slow kinetics for H_2 uptake and release. The thermodynamics dictates that relatively high temperatures must be



Appl. Phys. A (2016) 122:85
DOI 10.1007/s00339-016-9601-1

Applied Physics A
Materials Science & Processing

INVITED PAPER

Mg-based compounds for hydrogen and energy storage

J.-C. Crivello[1] · R. V. Denys[2] · M. Dornheim[3] · M. Felderhoff[4] · D. M. Grant[5] ·
J. Huot[6] · T. R. Jensen[7] · P. de Jongh[8] · M. Latroche[1] · G. S. Walker[5] ·
C. J. Webb[9] · V. A. Yartys[2]

Received: 29 September 2015 / Accepted: 3 January 2016

Abstract Magnesium-based alloys attract significant interest as cost-efficient hydrogen storage materials allowing the combination of high gravimetric storage capacity of hydrogen with fast rates of hydrogen uptake and release and pronounced destabilization of the metal–hydrogen bonding in comparison with binary Mg–H systems. In this review, various groups of magnesium compounds are considered, including (1) RE–Mg–Ni hydrides (RE = La, Pr, Nd); (2) Mg alloys with *p*-elements (X = Si, Ge, Sn, and Al); and (3) magnesium alloys with *d*-elements (Ti, Fe, Co, Ni, Cu, Zn, Pd). The hydrogenation–disproportionation–desorption–recombination process in the Mg-based alloys ($LaMg_{12}$, $LaMg_{11}Ni$) and unusually high-pressure hydrides synthesized at pressures exceeding 100 MPa ($MgNi_2H_3$) and stabilized by Ni–H bonding are also discussed. The paper reviews interrelations between the properties of the Mg-based hydrides and *p*–*T* conditions of the metal–hydrogen interactions, chemical composition of the initial alloys, their crystal structures, and microstructural state.

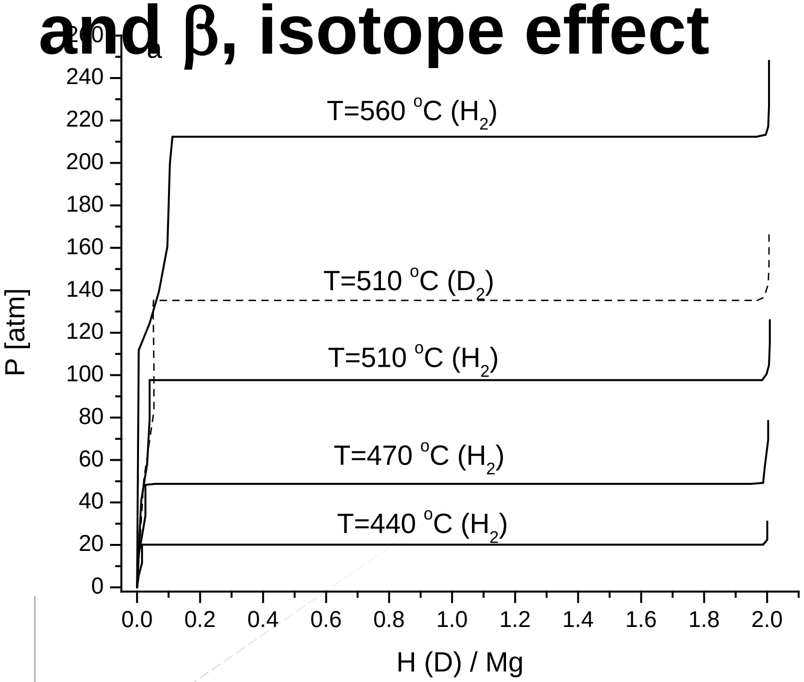
> 120 REFERENCES IN SCOPUS (2016-2018)

Mg-H and Mg-D systems

SYNTHESIS: DIRECT – 200 bar H_2 + 570 °C – 60 % (1951)

PYROLYSIS OF ETHYL MAGNESIUM HALIDE (1912)

Flat plateaux; No hysteresis; Small homogeneity ranges of α and β, isotope effect



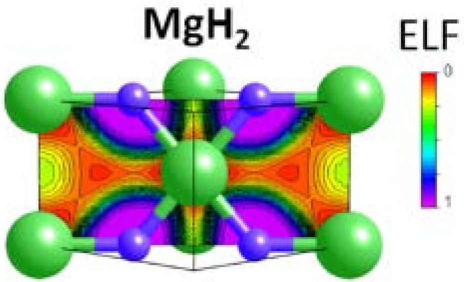
Stampfer J.F.et al. in 1960:
J Amer Chem Soc **82** (1960) 3504

ΔH_{des} = 75 kJ/molH_2

ΔS_{des} = 135 J/molH_2/K

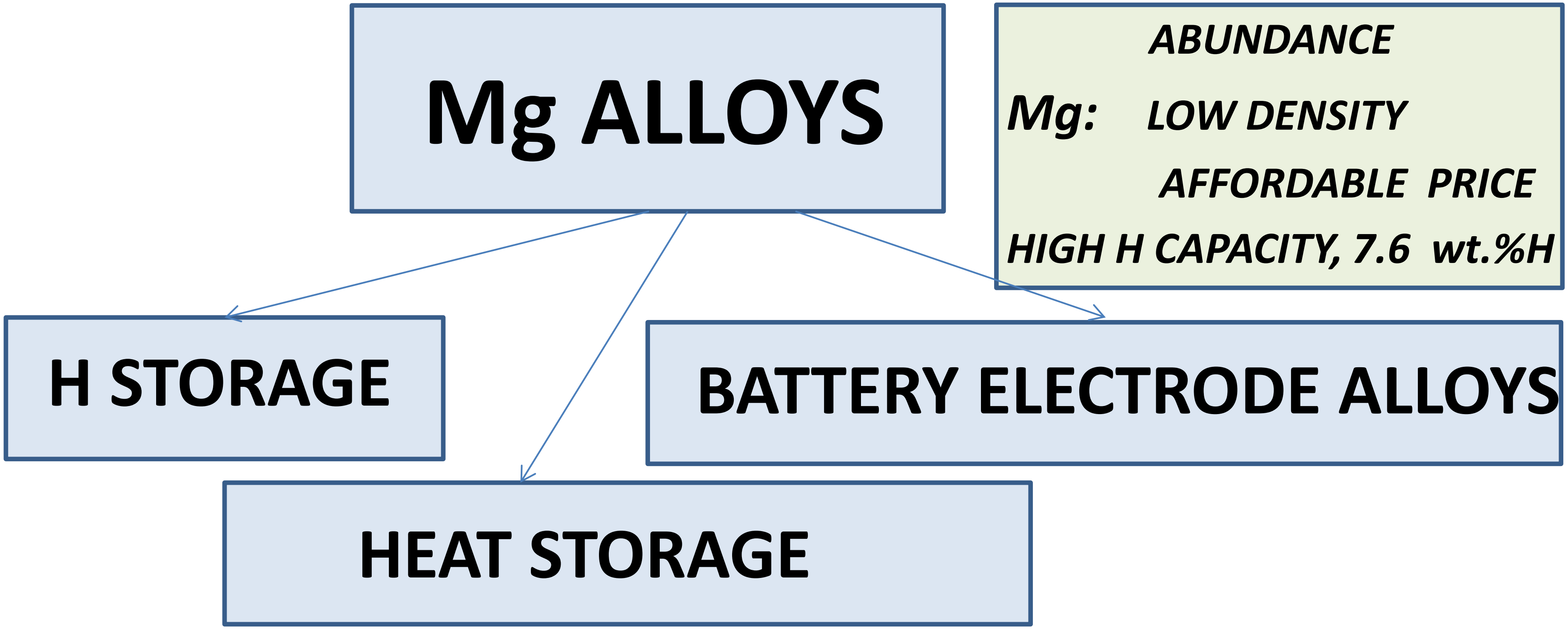
MgH_2 1 bar @ 277 °C

10 bar @ 370 °C



Strong covalent contribution to Mg-H bonding

J.C. Crivello, Appl. Phys. A: Materials Science and Processing **122 (2)** (2016) : 97, pp. 1-20



Mg ALLOYS

Mg: ABUNDANCE
LOW DENSITY
AFFORDABLE PRICE
HIGH H CAPACITY, 7.6 wt.%H

H STORAGE

BATTERY ELECTRODE ALLOYS

HEAT STORAGE

EFFECT OF MAGNESIUM ON THE STRUCTURE, THERMODYNAMICS AND KINETICS OF THE METAL-HYDROGEN INTERACTIONS

IFE Institute for Energy Technology

TOPICS OF REVIEW PAPER

- HISTORICAL OVERVIEW
- NANOSTRUCTURED MgH_2
- MA @ RBM. MECHANOCHEMISTRY of Mg in H_2
- CATALYSIS OF DE/HYDRIDING
- DESTABILISATION of MgH_2
- Mg-H SYSTEM AT HIGH PRESSURES. THEORY AND EXPERIMENTS
- NEW TERNARY Mg CONTAINING H STORAGE MATERIALS
- NON DIRECT THERMAL DESORPTION
- CYCLING of MgH_2
- MAGNESIUM COMPOUNDS FOR THERMAL ENERGY STORAGE
- SYSTEM DEVELOPMENT
- SUMMARY, OUTLOOK AND FUTURE PROSPECTS

EFFECT OF MAGNESIUM ON STRUCTURE AND BONDING IN MULTICOMPONENT HYDRIDES

(a) Mg substitution of Rare Earth metals;

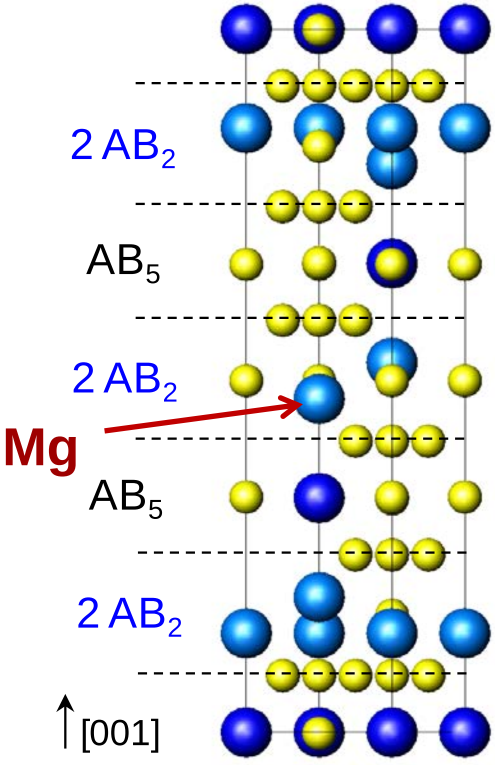
(a) Mg as an individual component of ternary intermetallics;

(a) Mg forms Mg^{2+} ions while transition metals Ni, Co, Fe form compex anions **$[NiH_4]^{4-}$**, $[CoH_5]^{4-}$ and **$[FeH_6]^{4-}$**

Effect of Mg ⇒ La substitution

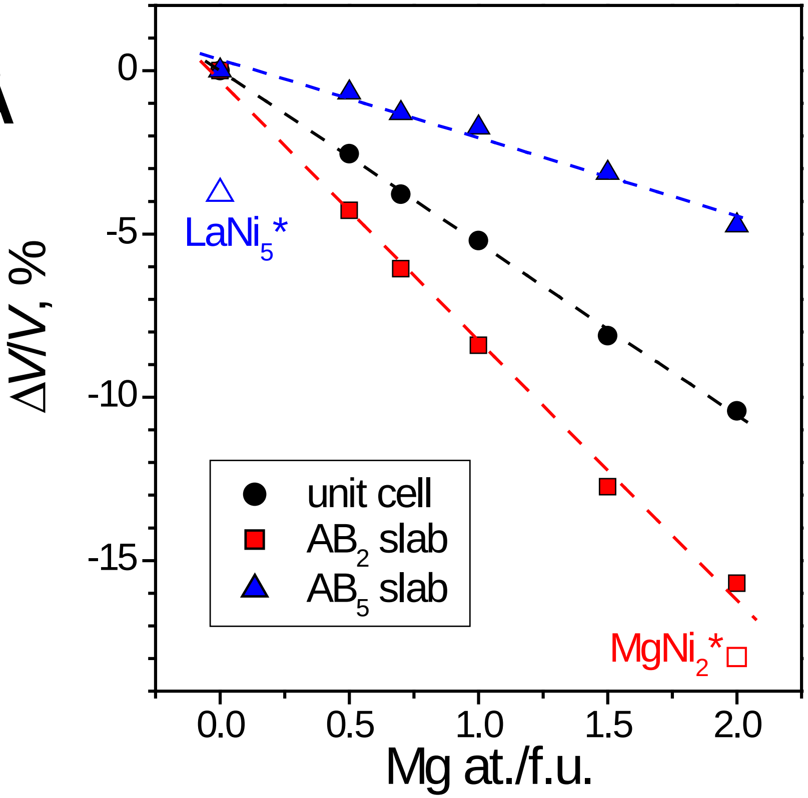
La 1.87 Å
Mg 1.60 Å

$LaNi_3 \rightarrow LaMg_2Ni_9$



r(La)=1.87 Å
r(Mg)=1.60 Å

Volume of structure fragments in $La_{3-x}Mg_xNi_9$ vs. $LaNi_3$

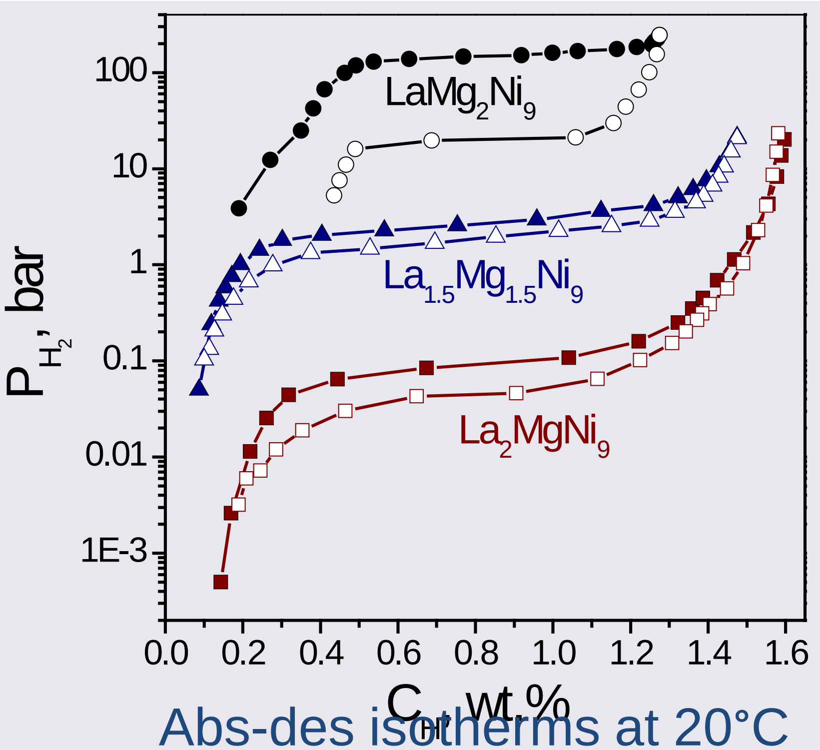


Mg subslitutes La exclusively in the AB_2 layers. Significant shrinking of both AB_2 and AB_5 layers

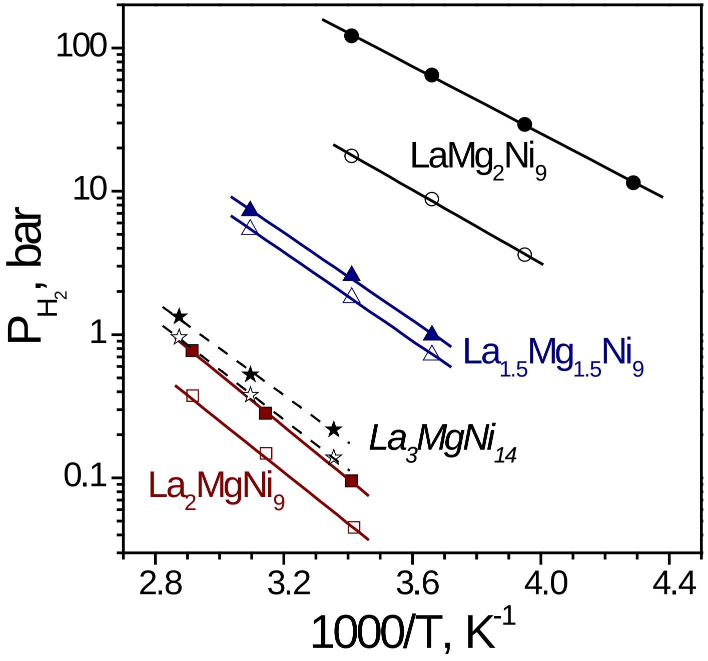
Yartys, Denys, 2016

THERMODYNAMICS of $La_{3-x}Mg_xNi_9$-H_2 SYSTEMS

Van't Hoff plots



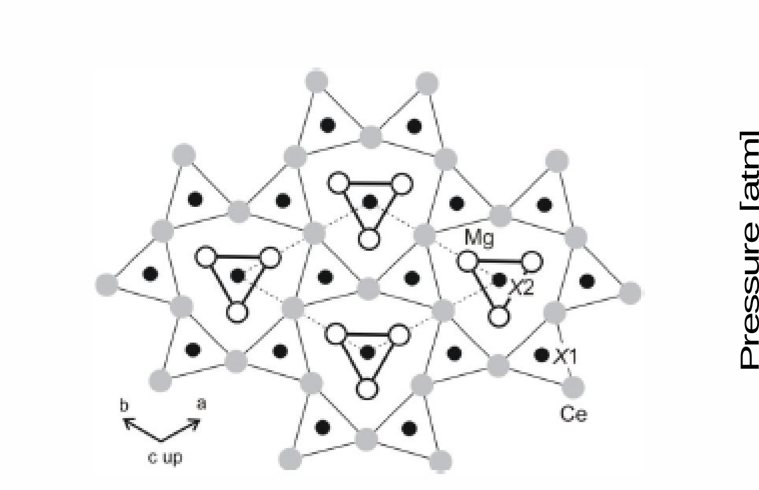
Abs-des isotherms at 20°C



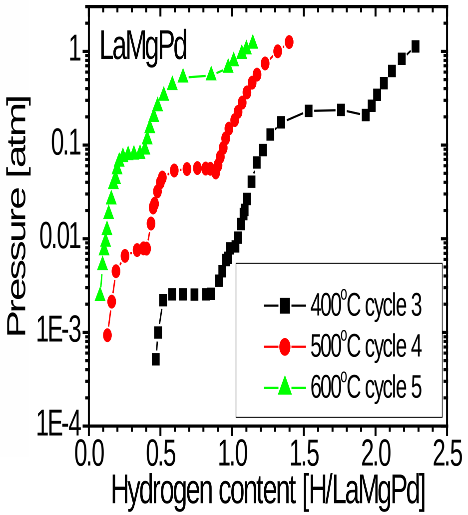
Yartys, Denys, 2016

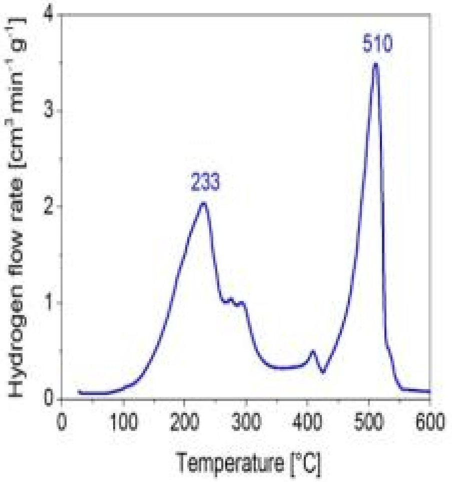
Dramatic change of H_2 pressures, from 0.05 to 150 bar when Mg content changes from x = 1 to x = 2

TERNARY Mg-CONTAINING INTERMETALLIC HYDRIDES: LaMgPdH_5

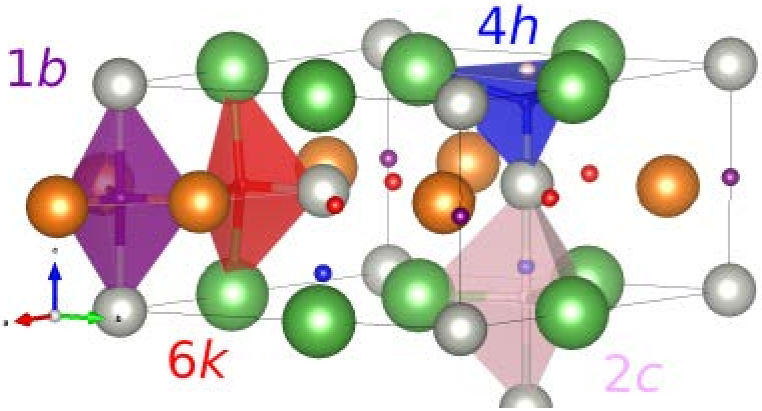


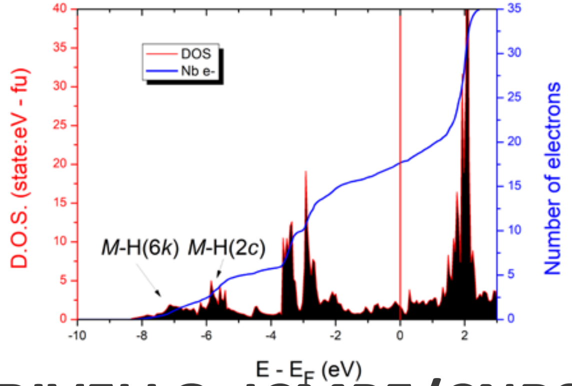
ZrNiAl type





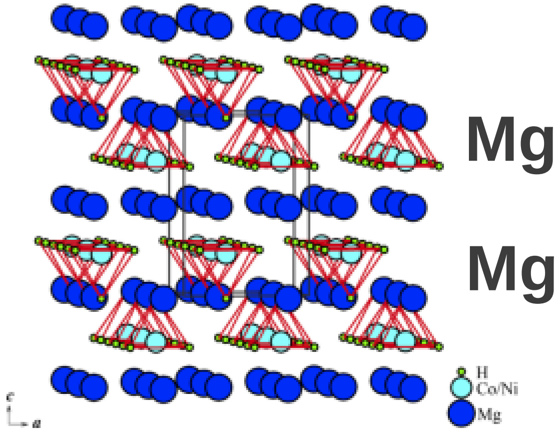
I. JACOB, Ben-Gurion University, MH2018





J.-C. CRIVELLO, ICMPE/CNRS, 2018

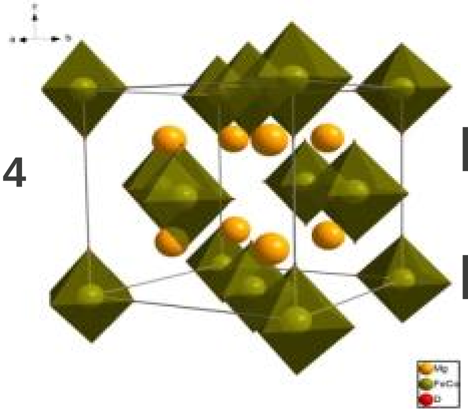
MIXED TRANSITION-METAL COMPLEX Mg-BASED HYDRIDES



$Mg_2Ni_{0.5}Co_{0.5}H_{4.4}$

Mg_2CoH_5 type

Yu. Verbovytskyy, J. Zhang, F. Cuevas, V. Paul-Boncour, I. Zavaliy. *JALCOM* **645** (2015) S408.

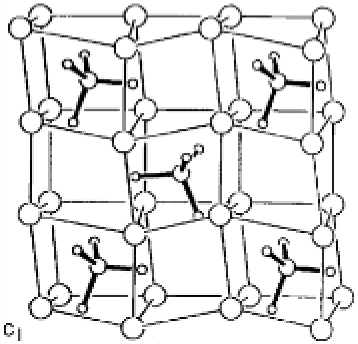


$Mg_2Fe_xCo_{1-x}H_y$

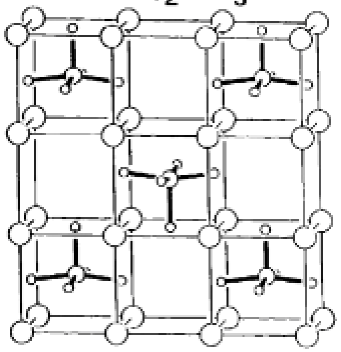
K_2PtCl_6 type

J. Barale, S.Deledda, E.M. Dematteis, M.H. Sørby, M. Baricco, B.C. Hauback, to be submitted.

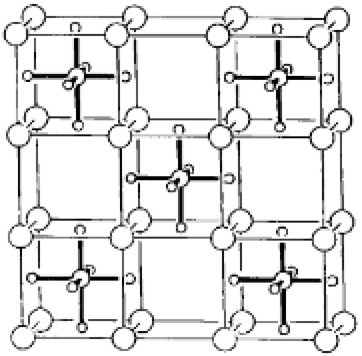
Mg_2NiH_4

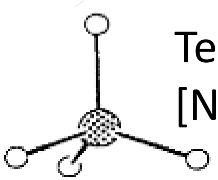


Mg_2CoH_5

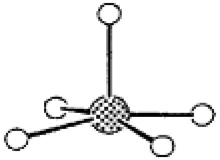


Mg_2FeH_6

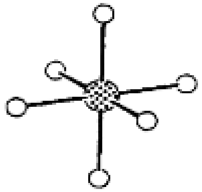




Tetrahedral
[NiH4]$^{4-}$



Square pyramidal
$[CoH_5]^{4-}$



Octahedral
$[FeH_6]^{4-}$

EASY HYDROGENATION AND MgH_2 DECOMPOSITION

CATALYSIS

Catalytic effect is related to:

(1) Type of additive having specific catalytic influence

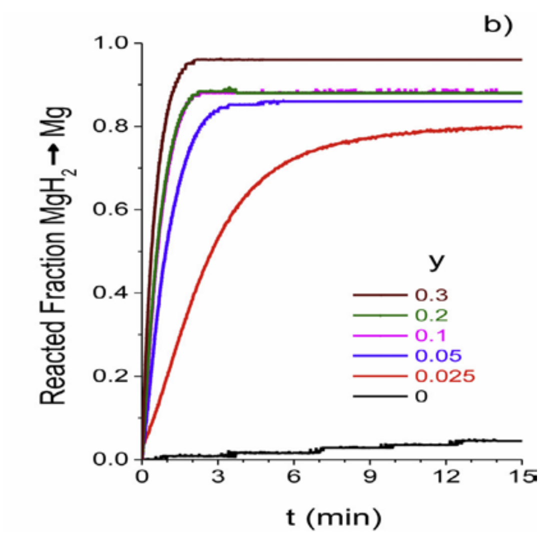
(2) Particle size and distribution of catalyst

(3) Structural stability of catalyst during hydrogenation-dehydrogenation cycling

CATALYSERS: carbon materials, metals and intermetallics, transition-metal compounds (oxides, halides, hydrides, carbides, nitrides, and fluorides)

Mg-Ti, Mg-C and Mg-Ti-C

Mg-Ti

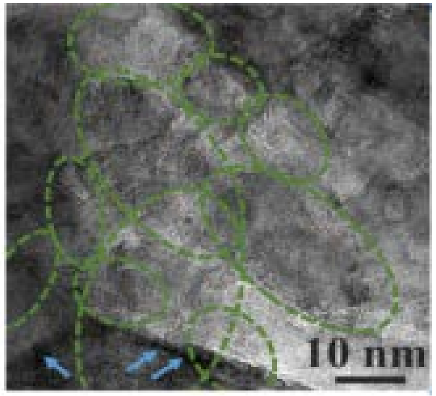


H desorption from (1-y)MgH2-TiH2 nanocomposites @ 573 K 30 % TiH_2

4 wt.% H

Cuevas, Latroche, 2018 (IJHE)

Mg-C

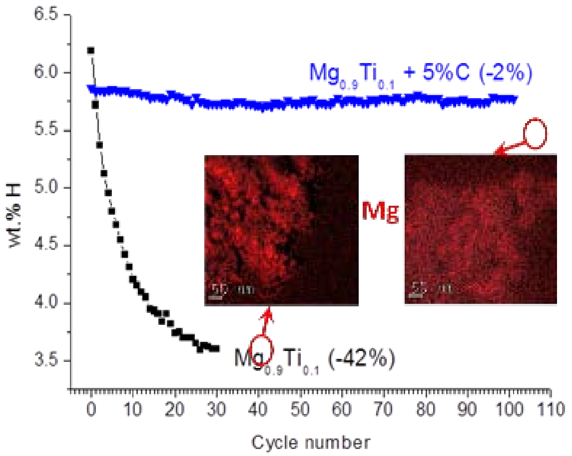


Effect of Mg with MWCN. Anisotropic chains of carbon.

high thermal conductivity + fast H diffusion.

Rabkin, IJHE, 2016 2017

Mg-Ti-C



Mg90Ti10 + 5% C

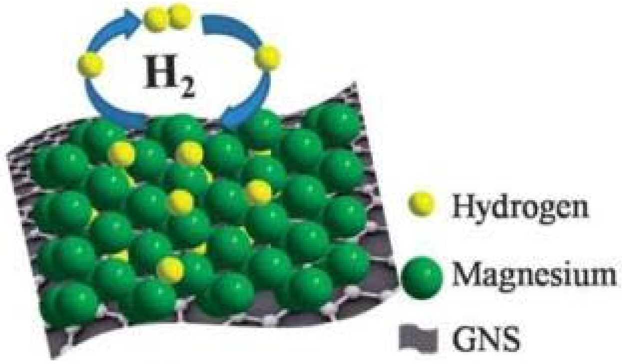
Outstanging cycling perfomance

6 wt.% H

Lototsky, Yartys 2018 (JMC A, 2018)

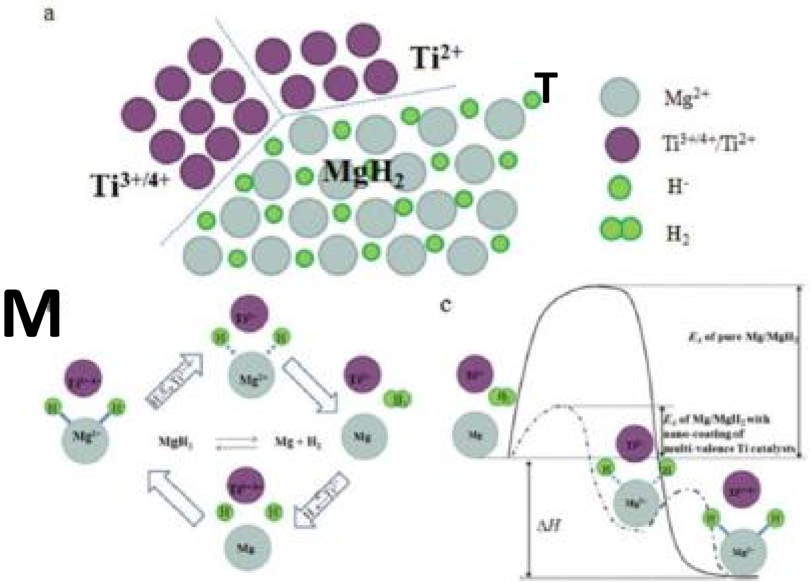
MECHANISM

CARBON



HYDROGEN TRANSFER TO Mg

TITANIUM

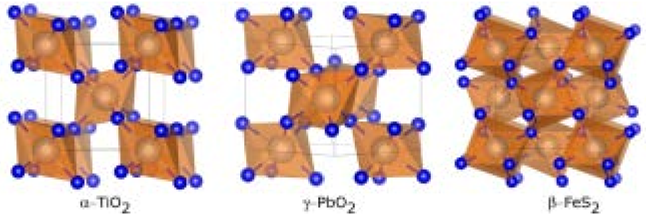


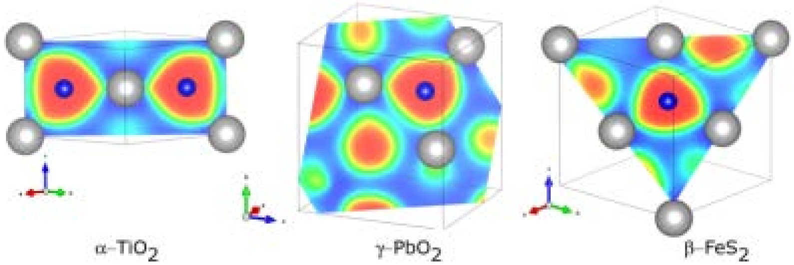
DECREASED ACTIVATION ENERGY OF HYDROGEN DESORPTION

MIN ZHU, HUI WANG, 2018

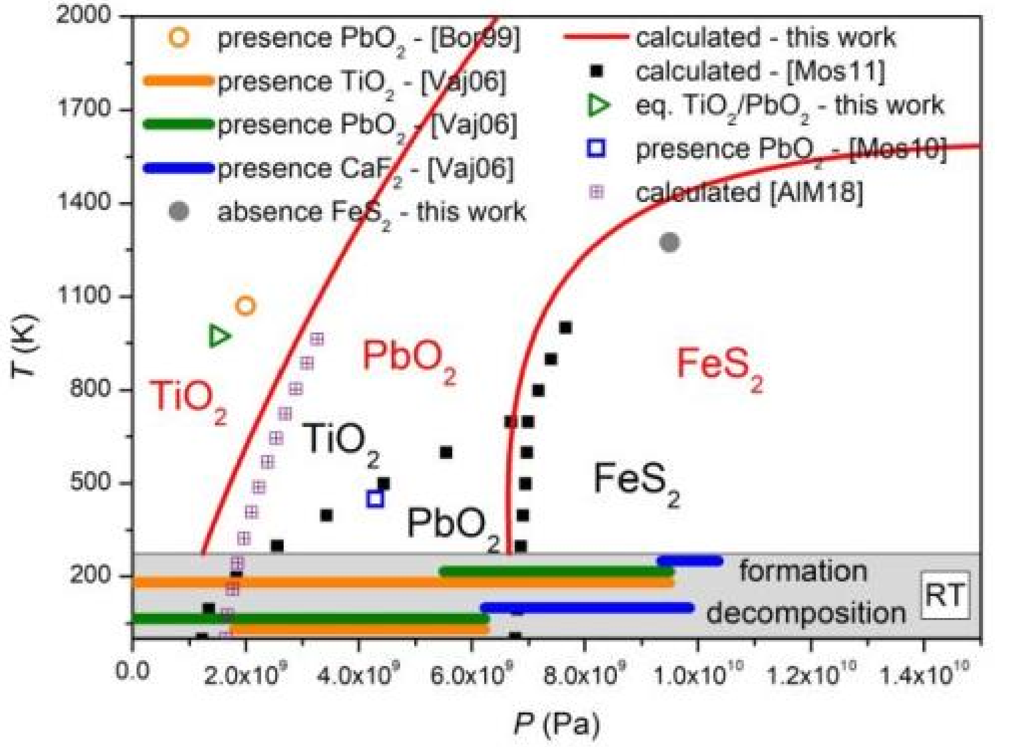
DESTABILISATION OF MgH_2

POLYMORPHIC MODIFICATIONS OF MgH_2



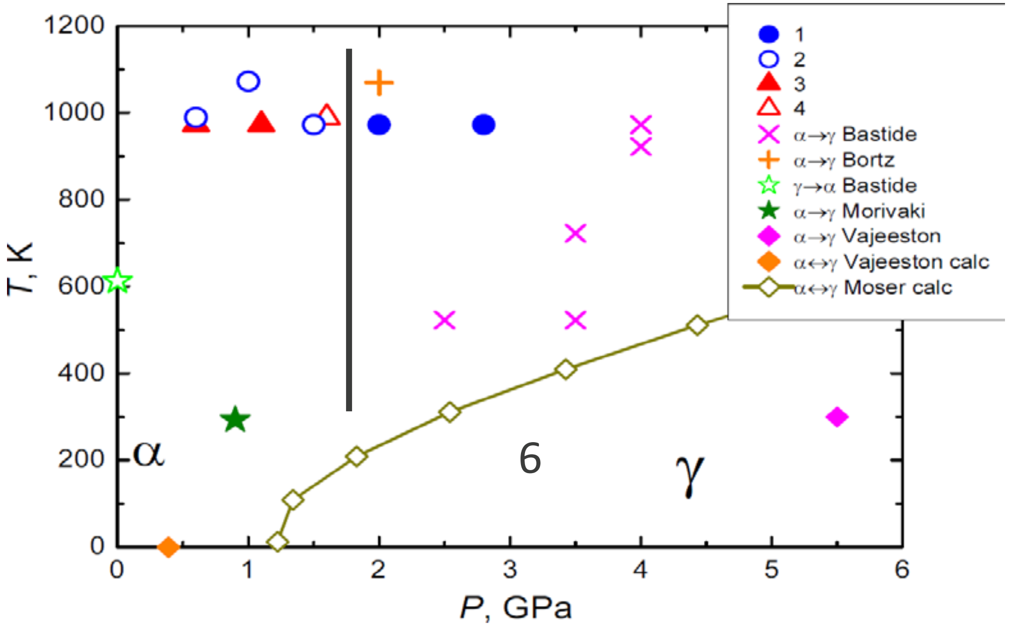


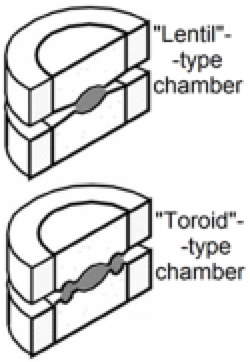
Mg-H BONDING in MgH_2

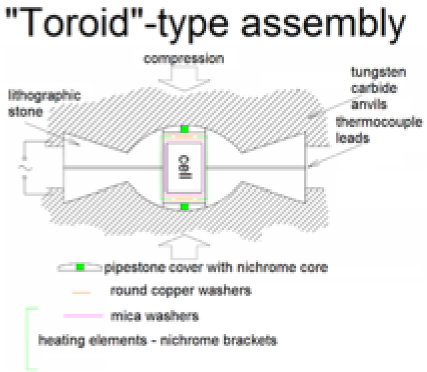


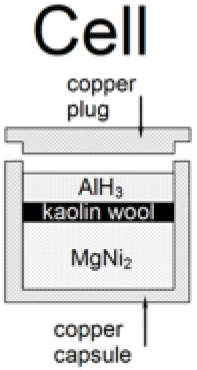
Bourgeois, Crivello, Joubert (2018)

EXPERIMENTAL STUDIES OF Mg-H SYSTEM AT HIGH PRESSURES (600 kBar)





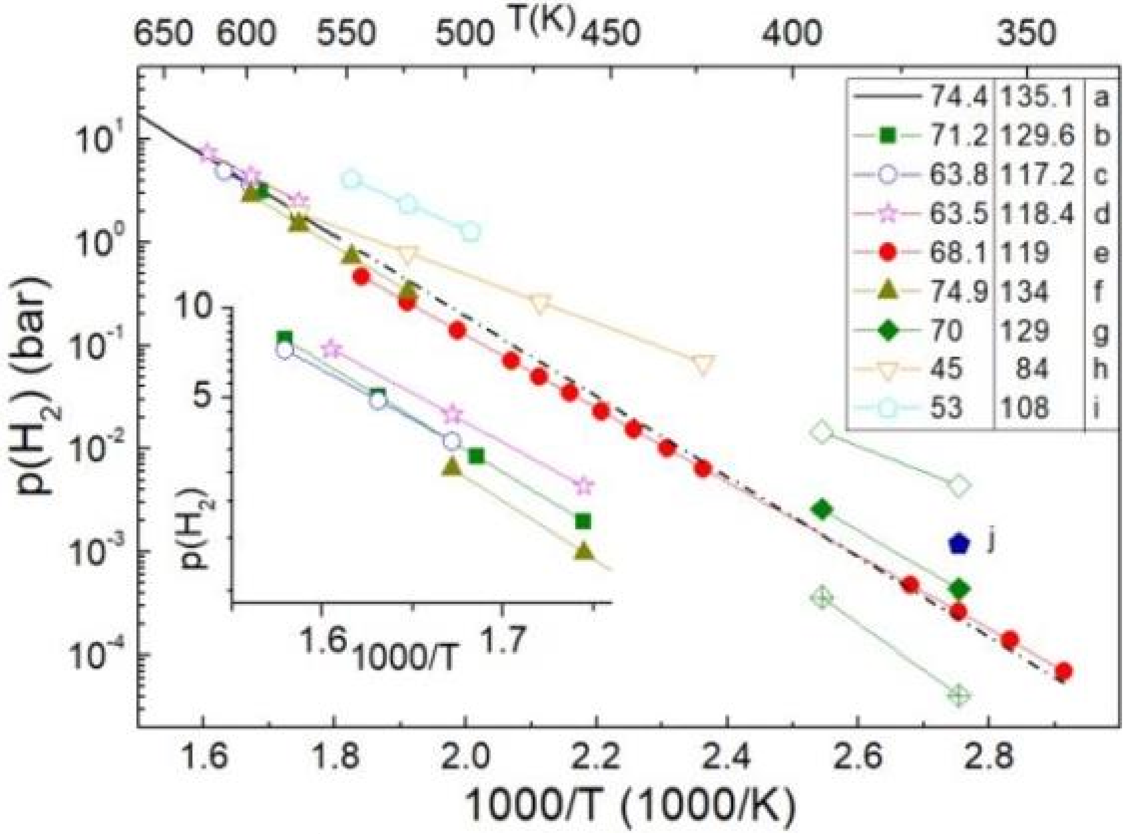




Antonov, Kuzivnikov (2018)

van ‘t Hoff plots calculated data for Mg-based nanomaterials

High ratio A/V between the total interface area (A) and volume (V) is a distinct feature



L. Pasquini, P de Jongh, 2018

BULK Mg (a)

NANOMATERIALS:

Smallest size:

Thin film 2 nm (j)

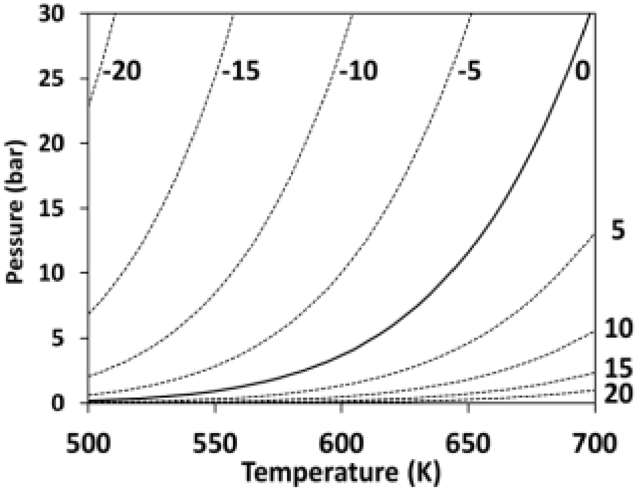
Nanocrystallites 2 nm (b)

Mg 3 nm NPs in carbon scafolds (c)

STRONG HYSTERESIS IN MANY CASES ⟶ $p_{eq} = (p_{abs} \cdot p_{des})^{1/2}$

p_{eq} **shows only small changes compared to bulk Mg**

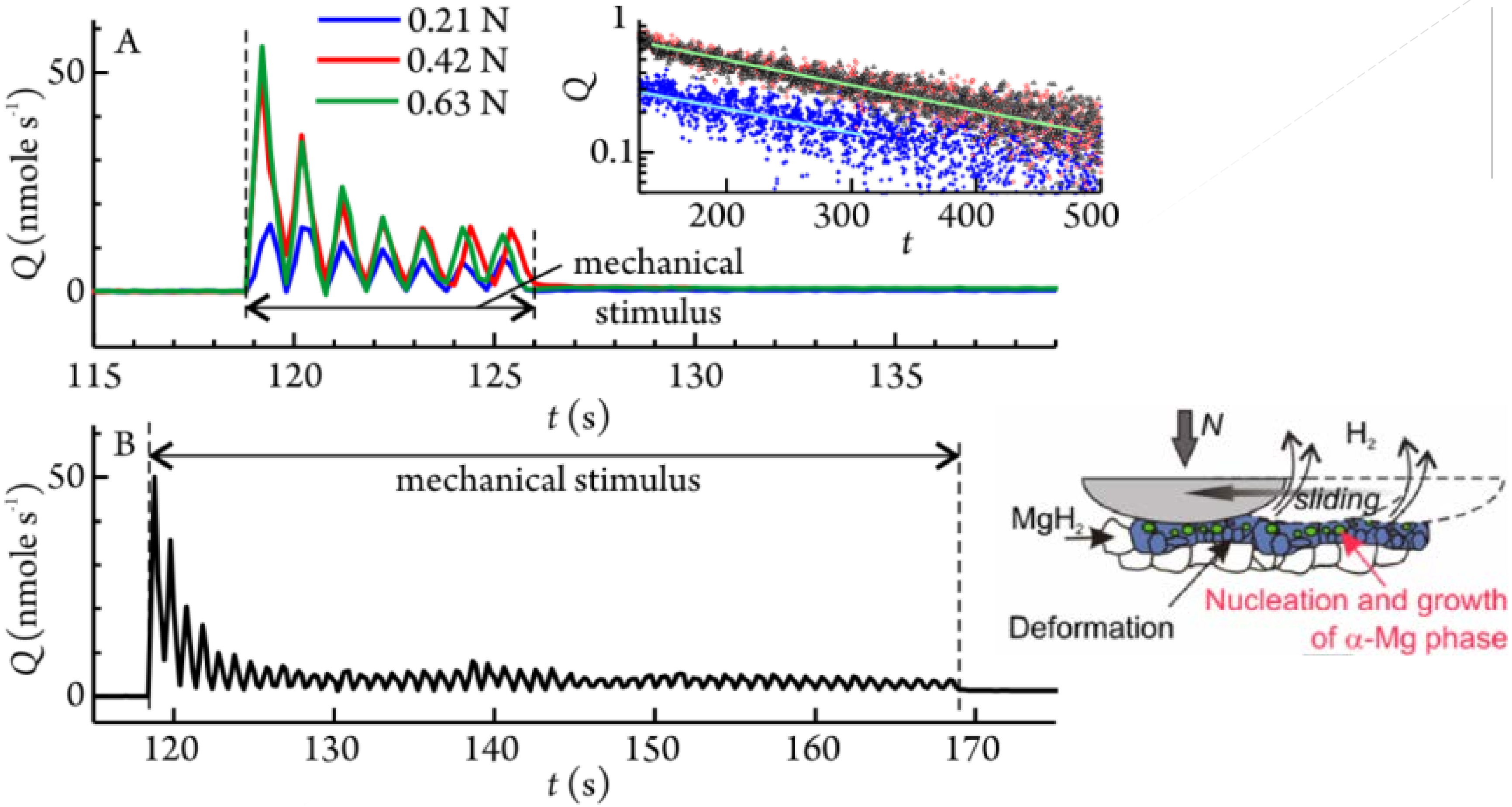
Particles of less than 1.3 nm are required to have considerable shifts in the equilibrium temperature during decomposition of MgH_2



Calculated driving forces for hydrogen absorption/desorption in Mg as a function of temperature and pressure.
Control over backpressure of hydrogen required during kinetics measurements,

M. Baricco, 2018

NON DIRECT THERMAL DESORPTION METHODS

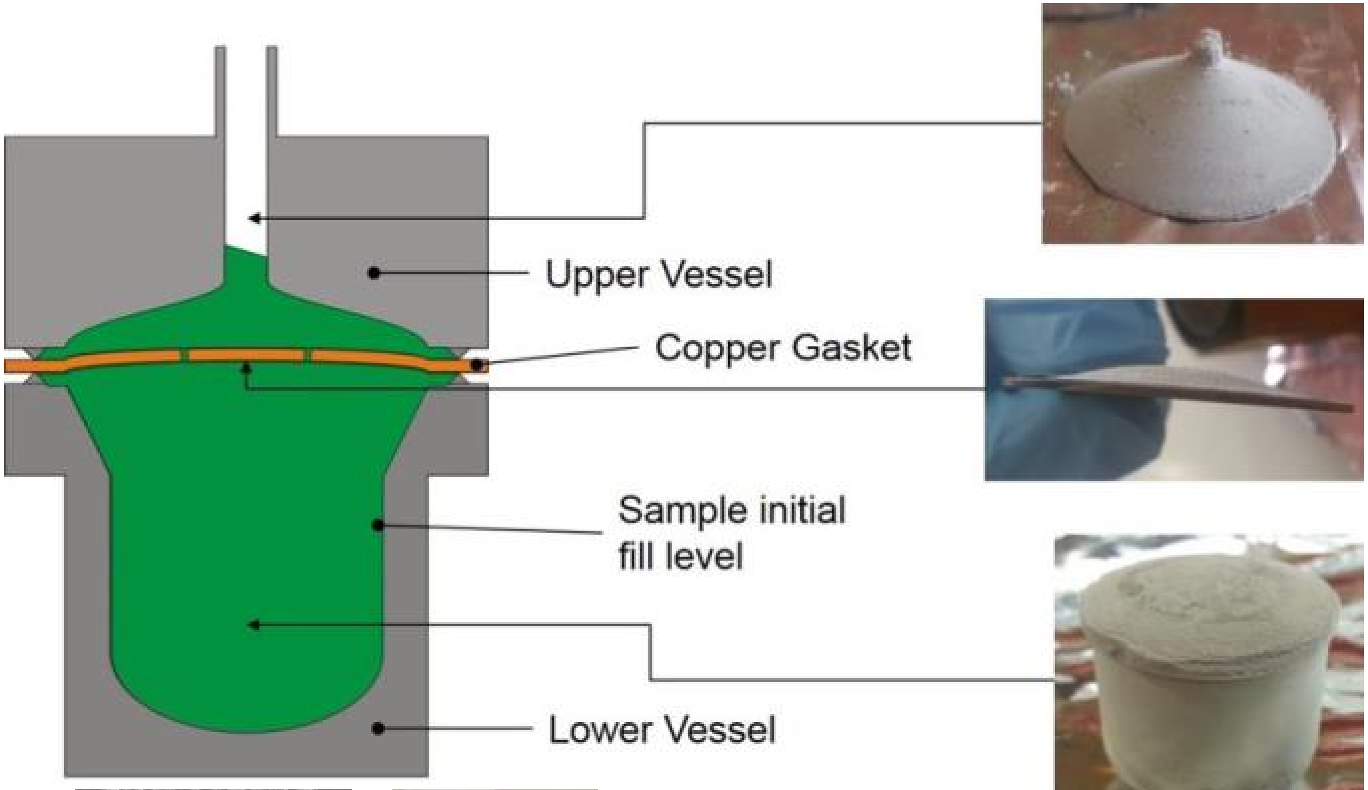


Mechanical bias has been applied to drive tribochemical decomposition under mechanical micro-deformation of MgH_2 . **MgH_2 decomposition occurs by an instantaneous (t ~ s) non-thermal H-release at RT during mechanical treatment**

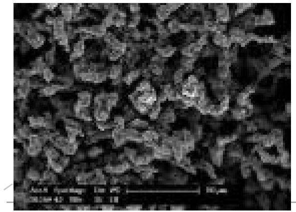
R. Nevshupa, **J.R. Ares**, J.F. Fernández, A. del Campo, E. Roman. Tribochemical Decomposition of Light Ionic Hydrides at Room Temperature, *J. Phys. Chem. Lett.* 6(14) (2015) 2780-2785.

IMPROVING CYCLE LIFE

MAGNESIUM HYDRIDE AS A POWDER: CYCLING PROPERTIES - GOAL: HIGH POROSITY GIVES BETTER KINETICS AND THERMAL PROPERTIES



Expanding structure places additional stresses on the walls of reactors and impede the material kinetics



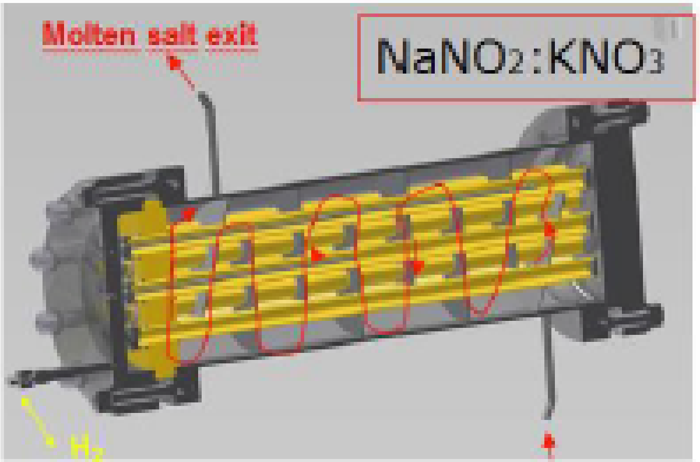
50 CYCLES @ 400 °C FORM A POROUS STRUCTURE

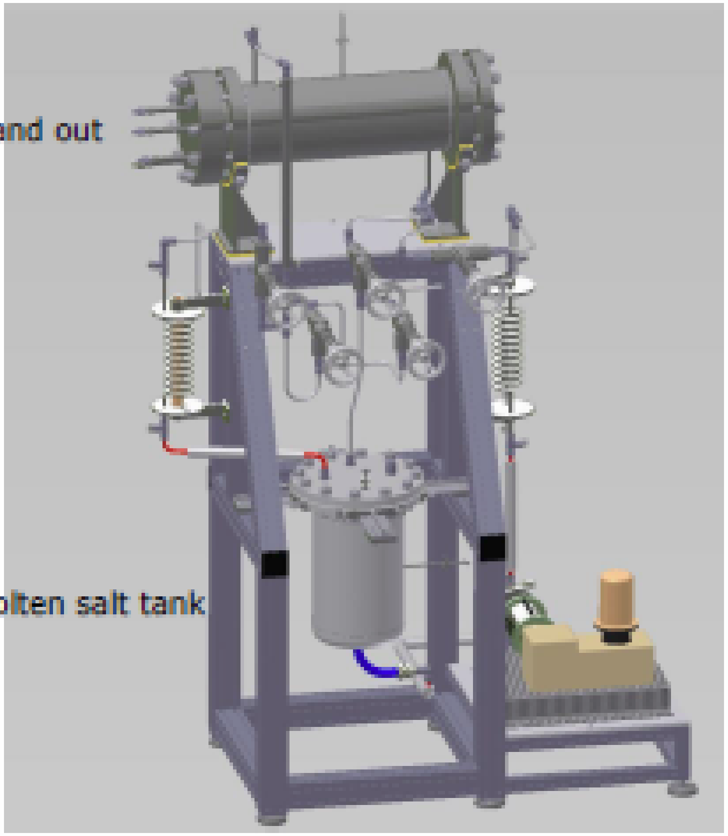
Grant et al, 2018

THERMAL STORAGE

Demonstration of Heat Storage using Mg_2FeH_6 at T = 500 °C

$$2\,Mg + Fe + 3\,H_2 \rightleftharpoons Mg_2FeH_6 \qquad \Delta H = 77\ kJ\ mol^{-1}\ H_2$$





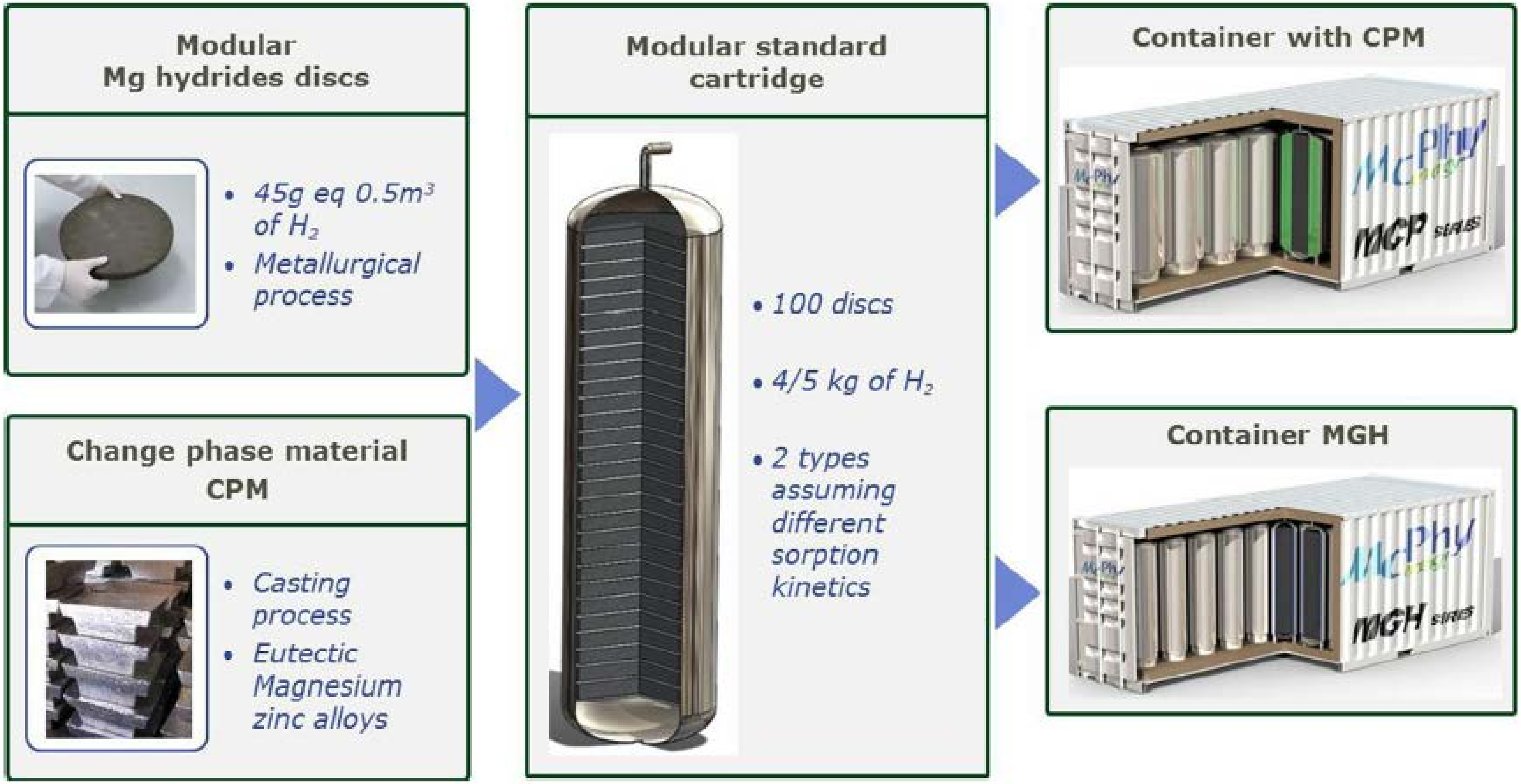
Mg_2FeH_6 Parameters:

- $V_{2Mg\text{-}Fe}$ = 4.5 l
- $\rho_{2Mg\text{-}Fe}$ = 1085 g/l
- $m_{2Mg\text{-}Fe}$ = 4830 g
- $x_{H_2,\ real}$ = 5 %
- m_{H_2} = 254 g
- $m_{Mg_2FeH_6}$ = 5084 g
- $\Delta^R H$ = 77.2 kJ/mol$_{H_2}$
- Q_{target}= 2.7 kWh

R. Urbanczyk *et al.*, *Int. J. Hydrogen Energy*, **2017**, *42*, 13818.

H STORAGE SYSTEMS

MgH2 BASED H STORAGE @ McPhy



Modular Mg hydrides discs

- 45g eq 0.5m^3 of H_2
- Metallurgical process

Change phase material CPM

- Casting process
- Eutectic Magnesium zinc alloys

Modular standard cartridge

- 100 discs
- 4/5 kg of H_2
- 2 types assuming different sorption kinetics

Container with CPM

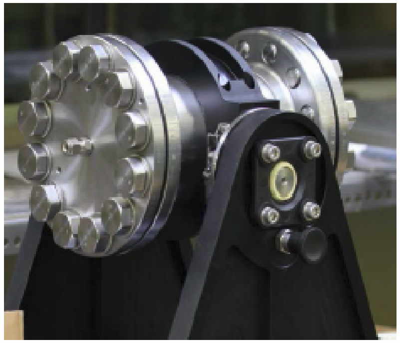
Container MGH

*Michel Jehan, Daniel Fruchart, JALCOM **580** (2013) S343*

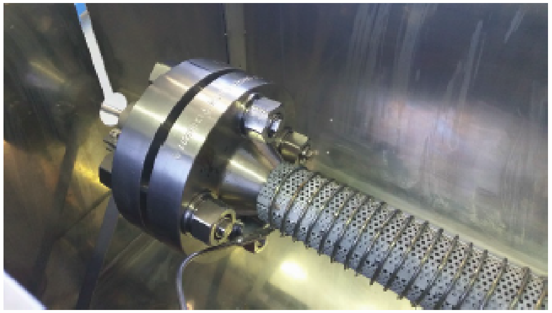
MgH_2 / $LiBH_4$ tank designs

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

- 1st generation high temperature tank: tube and shell design
- Due to filtering system, phase separation happened; temperature limitations



- 2nd generation: large diameter, designed for heat transfer studies



- 3rd generation: under testing; improved temperature homogeinity. To be coupled to SOFC.

- Highest gravimetric capacity : factor 5 x over room temperature hydrides
- Low pressure (below 50 bar), operational temperature: > 300 °C [1]

Jose Bellosta von Colbe, Giovanni Capurso, Martin Dornheim

OUTLOOK

We review a field of magnesium-based materials, including alloys, compounds and composites. This is expected to bring new important developments resulting in important applications.

This review contains a broad variety of topics of fundamental and applied studies of magnesium based systems and a review of the frontiers of both experimental and theoretical research.

Currently, magnesium-based materials attract much attention in hydrogen storage, are used for storage of concentrated solar heat with high energy densities and in metal hydride batteries.

Furthermore, In future, novel types of magnesium batteries may replace the currently very successful lithium batteries. This clearly highlights the relevance of continuing research and developments within the area of magnesium based materials.

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