MgH$_2$ nano-structured powders for hydrogen storage
MCP Mg-Serbien SAS
Production unit at Romans (Drôme), 90 km south Lyons, France

Company developed by M. Jehan 1995

MCP Mg-Serbien produces granules, powders and chips of pure Mg and its alloys, aluminum and other alcaline-earth metals.

Specific sieving of reacting powders (e.g. nuclear application powders)
Continuous production 24 hours a day / 6 days a week.

Production team: 22 personnes on a certified site (DRIRE).
Mg present capacity: 6 000 M tons
Equipements and processes at MCP Mg-Serbien - Romans

- Production up to 500 tons a year
- of granules and powders
- Morphologies suited for steel production and chimistry (metal-organics, vitamines)
- Granules of Mg-alloys for “Thixomoulding”

- One of the two large facilities in Western-Europe for transformation of Mg into fines particles
- Automatised equipements
- Laboratory complet for characterisation by laser granulometer
Production of Mg hydrides

- Cooperation with Centre National de la Recherche Scientifique – Grenoble to synthesise and produce activated Mg-hydride for reversible hydrogen storage
- Goal: industrial scale production

- European Projects
  HYSTORY « 6th PCRD : Energy, Environment and Sustainable Development » High Energy ball-milling of nanostructured MgH₂
  NESSHY « 7th PCRD Novel Efficient Solid Storage of Hydrogen » Production of MgH₂ powders with catalysts
  International patent MCP-CNRS

- Other Projects
- Requests: More than 1000 MTons a year of MgH₂
- French Label ENERDIS
High Energy Industrial Ball-Milling

Mecanosynthesis of MgH₂ with transition metal under controlled atmosphere

Industriel scale production (on request)
Other équipements

Isostatic cold pressing up to 4000 bars

Pilot ball miller in liquid or gas

Controlled atmosphere glove boxes
MgH$_2$ nano-structured powders for hydrogen storage

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Stockholms Universitet S
Institut For Energiteknikk N
University of Fribourg CH
University of Birmingham UK
Vrije Universiteit Amsterdam NL
CNRS Grenoble F
Daimler Chrysler AG D
GKSS Geesthacht GmbH D
University of Iceland IS
Johnson Matthey PLC UK
ForschungZentrum Karlsruhe D
Max-Planck MPI-MF D
Technical University Denmark DK
METU Ankara T
INETI Ankara TR
IFW Leibniz Gemeinschaft D
Delft University of Technology NL
Southwest Research Institute USA

Fr0651478
Fr0601615
Why store hydrogen?

- Oil: cost increases, resources decrease, greenhouse effect…
- Renewable energies (solar, wind,…): irregular availability

**Hydrogen: Energy-carrier for the future?**

- Electric energy storage
- Fuel Cell
- ICE

Hydrogen storage in safe conditions
High gravimetric density of energy (142 MJ/kg)
Reversible Metal Hydrides

- **Compressed gas** (350-700 bars)
- **Cryogenic liquid** (20 K)
- **Chemical hydrides**

+ High volume density of hydrogen
+ Safe solution (low pressure, endothermic release)
+ Large-scale production
+ Purity of Hydrogen (Fuel Cells)

- Low weight density!

<table>
<thead>
<tr>
<th></th>
<th>kg H₂ / m³</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ gas 700 b</td>
<td>62</td>
<td>100 *</td>
</tr>
<tr>
<td>H₂ liquid</td>
<td>70</td>
<td>100 *</td>
</tr>
<tr>
<td>LaNi₅H₆</td>
<td>123</td>
<td>1.4</td>
</tr>
<tr>
<td>Ti-V-Cr</td>
<td>205</td>
<td>3.5</td>
</tr>
<tr>
<td>AlNaH₄</td>
<td>96</td>
<td>7.5</td>
</tr>
<tr>
<td>MgH₂</td>
<td>106</td>
<td>7.6</td>
</tr>
</tbody>
</table>

* not comprising mass of tank
Why metal hydrides? Why MgH$_2$?

Advantages with Mg:
- Mg is the 7th most abundant element on earth
- Mg is cheaper than... Al
- Mg metallurgy is easy
- Mg is non-toxic
- Mg is re-cyclable
- MgH$_2$ is mono-metal element system: no demixtion
- MgH$_2$ uptake is 7.6 w%

Difficulties with Mg:
- H-reaction kinetic are said low, but...
- Temperatures of reaction are high, but...
MgH₂ towards nano-structured powders

Mg + H₂ ↔ MgH₂

+ High weight storage capacity (7.6 wt. % H₂)
- High thermodynamic stability
  T > 300°C, but heat flow control...
  - Slow diffusion kinetics, but...

Ball-milling (BM) with catalysts (transition metals or oxides)
Co-milling process vs BM time

MgH$_2$ MCP + 5 \% at. V (40 $\mu$m)

Large impact of the milling time, especially at desorption

Optimum $\approx$ 20 hours milling time with catalysts
MgH$_2$ and M transformation on BM

- High density of defects
- Reduction to nanosize MgH$_2$ crystallites
- Progressive MH$_x$ formation from MgH$_2$

$V \rightarrow V_2H \rightarrow VH_{0.81}$
$Nb \rightarrow NbH_{0.89} \rightarrow NbH_2$
$Ti \rightarrow TiH_{1.7} \rightarrow TiH_{1.7} + TiH_{1.92}$

Interfaces between MgH$_2$ grains and M particles
Microstructural evolution on BM

- **Granulometry measurements**

  Starting powder: 20 – 80 µm
  After 15 min. milling time: 1 – 10 µm
  No further evolution

- **Crystallites size of the $\beta$-MgH$_2$**

  After 15 min. milling time: 30 nm
  Further crystallites size reduction with increasing milling time

<table>
<thead>
<tr>
<th>Milling Time</th>
<th>Crystallite sizes (nm)</th>
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</thead>
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<tr>
<td>15 min</td>
<td>29,(3)</td>
</tr>
<tr>
<td>30 min</td>
<td>14,(2)</td>
</tr>
<tr>
<td>1 h</td>
<td>12,(2)</td>
</tr>
<tr>
<td>5 h</td>
<td>10,(9)</td>
</tr>
</tbody>
</table>

Hydrogen sorption properties not correlated to powder grain size, but to the crystallites size.
Microstructure evolution on cycling

The high density of defects disappears after D/H cycles.
Recrystallisation of hexagonal single crystallites of Mg.

Fast hydrogen diffusion results from the very large amount of boundaries developed between nanometric crystallites.
In-situ neutron diffraction study (ILL - D20)

In-situ hydrogenation (T ~ 280°C, P = 2 MPa)

ε - NbD$_{0.75}$ rapid formation prior to the MgD$_2$ formation

Role of the TM additives ~ “gates” favoring H$_2$ dissociation, then H diffusion
Up-scaling powder production
@ MCP-Serbien

1. Synthesis the MgH₂ precursors from Mg powder
2. Co-milling MgH₂ + M additives

Large scale energetic ball miller (25 l)
Batches of 1 kg of activated powders

Very reactive powder in air (to handle under Ar gas)

Patent FR 06-51478
Kinetics characterisation vs T

Absorption can be initiated at 50°C, reasonably faster at 150°C. 4% wt. in 1 minute at 200°C.

Highly reactive powders
Stability of the sorption properties on cycling

For 15 kPa:
- only 20 min at 240°C
- (1 h at 220°C)

MgH$_2$ MCP + 5 at.% V (40 µm) ZOZ Miller - 8 h
MgH₂ pilot tank development

Main problem = control of the heat transfers
- Strong exothermic Mg hydrogenation
- Low thermal conductivity of MgH₂ powder

Equilibrium conditions are immediately reached, thus stopping hydrogenation

120 g of MgH₂
(6 gr H₂ / 0.86 MJ)
Charging process (initial 280°C / 8 bars)

Without cooling fluid:

Huge increase of temperature (+ 80°C)
Total charging: 50 min. - 57 Nl (5 wt. %)

The central part of the tank follows the thermodynamic equilibrium up to the end of reaction, slowing H₂ absorption.
Charging process (starting 280°C / 8 b.)

With forced air as cooling fluid

Charge in 30 min. - 42 Nl (3.6 % wt.)

A cooling system reduces the tank loading-time
(managing the cooler is needed to complete the charge)
Numerical modeling

**Fluent® software**
- hydrogenation reaction
- H\(_2\) consumption
- heat generation
- thermal conductivity
- gradient of pressure

**Hydrogenation rate without cooling system**
- After 600 s
- After 2200 s
- After 5200 s

**Hydrogenation rate with forced air cooling system**
- After 400 s
- After 800 s
- After 1400 s
Fuel Cell - PAXITECH

120 g MgH₂ (6 gr H₂ / 0.86 MJ) : lightening for ~ 72 h.
Conclusion

• **Systematic investigation of the ball-milling process**
  - Activation role of the transition metal hydride directly evidenced

• **Highly reactive powders available by kg batches**
  - Stability of the sorption properties on cycling

• **Small scale tank tested with success (6 gr H\textsubscript{2} / 0.86 MJ)**
  - Loading process: P < 10 bars, starting at 150°C
  - Loading time strongly dependent of the cooling efficiency
  - Overall weight capacity to be optimized

New metallurgy routes (Severe Plastic Deformation: ECAP)
Pilot tank development 5 kg MgH\textsubscript{2} (250 gr H\textsubscript{2} / 36 MJ)
Recycling waste heat (SOFC, thermal engines, factories)
Fuel = Hydrogen

ICE
Thermal engine

PEMFC
Low temperature Fuel Cell

SOFHC
High temperature Fuel Cell

Hydrogen storage

Hydrogen

Gasoline

Gasoil/gas
High pressure
30 to 70 MPa

Cryogenic liquid
20 K

Solid hydrides

Reforming

MgH₂
Integrated Project:
Energy regenerating ICE / MgH₂ tank

~ 100 kg MgH₂ for ~ 250 – 300 km with ICE car

Low temperature 20°C metal hydride starter

MgH₂ Tank 300°C

Heat storage and Transfer unit

Heat exchanger

Hydrogen supply

Establish energy balance!

I.C.E.

Exhaust
Water vapour
What could be promising for Mg technologies?

10^8 ICE cars being equipped with MgH_2 tanks

250 kg MgH_2 for 700 km autonomy

20 years shift from gasoline to hydrogen civilisation

Needs for more than 10^6 tons Mg a year during more than 20 years!

NB - fuel cell: 0.3kW/kg, large volume, very expensive, very fragile, short life, resources of Pt, Rh ????
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