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# Improvements of hydrogen storage properties of Mg-based mixtures elaborated by reactive mechanical milling

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**Abstract**

The influence of mechanical grinding under hydrogen (Reactive Mechanical Grinding=RMG) on the chemical properties (crystallographic and phase composition) and on the hydrogen storage properties of Mg-based mixtures is examined. Different additives were studied such as: Co, YNi, oxides, BN. All these additives lead to an unequal improvement in the hydriding properties. For $Cr_2O_3$, the effect of both the morphology and crystallinity were studied by elaborating $Cr_2O_3$ by supercritical fluid process.

*Keywords:* Hydrogen sorption properties; Diffusion; Nucleation; Milling under hydrogen

## 1. Introduction

Among all the fuels of the future (to reduce pollution), it is now well established that hydrogen is one of the best. However, one of the problems to solve is the storage of hydrogen. The three main ways of storage are: under pressure (in the range 35–70 MPa), as liquid ($T$~20 K) or as intermetallic hydrides. The safety of the first two ways of storage is in question and the 'energetic cost' is not negligible (especially that of liquefaction). The third method offers the best safety but exhibits a low weight or volumic capacity. Magnesium is therefore a very promising candidate as it can store up to 7.6 wt.%. Unfortunately, the hydrogenation reaction is very slow and takes place at high temperature. A lot of research has been done to overcome these drawbacks and has been focused on two major directions: (i) the additions of various compounds (3d metal [1], intermetallics [2], oxides [3], etc.) and (ii) the use of mechanical grinding [4–6].

In this paper, the sorption properties of several Mg-based mixtures studied during the last 4 years and elaborated by RMG are reviewed and finally the results obtained with more 'exotic' addition compounds (BN and $Cr_2O_3$ elaborated by supercritical fluid process) are presented.

## 2. Experimental

The intermetallic compound YNi was prepared by melting pure Y and Ni in an arc furnace and annealing at 1073 K for 1 week. It was crushed and sieved under 100 μm for RMG experiments.

Eight grams of high purity elemental powders (i.e. Mg, Co, $Cr_2O_3$, $Yb_2O_3$, BN, YNi, etc.) were charged and sealed in cylindrical stainless steel containers together with 17 stainless steel balls of 10 mm in diameter. The vial was filled with hydrogen up to 1.1 MPa. The plateau rotation speed was 200 rpm and every 15 min of milling, the vial was recharged with hydrogen ($P$=1.1 MPa).

The samples were characterized by XRD, SEM, particle size analyser and electron microprobe analysis. The hydrogen sorption properties were measured by the Sievert's method. All these appliances and the mathematical methods used (Rietveld refinement, Mie theory, etc.) have been described previously [7,8].

The precursor used for the synthesis of $Cr_2O_3$ by supercritical fluid (named in the following $Cr_2O_3$ FSC) was the chromium acetyl acetonate and the fluid was $NH_3$.

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The supercritical conditions were $T=200\,^{\circ}\mathrm{C}$ and $P=20$ MPa. It has been shown that these compounds were completely amorphous and that the particle size was under 5 μm.

## 3. Results and discussion

### *3.1. Structural and chemical study*

The RMG of Mg-based mixtures results in the initiation of $MgH_2$ formation and then leads to great improvement in kinetic behaviour. Whatever the metallic compounds or intermetallic used as additives, the trend observed for the formation of $MgH_2$ during grinding is equivalent (i.e. about 10% of $MgH_2$ formed after 2 h and around 30–40% after 5 h). However, the addition of oxides increases the transformation of magnesium into $MgH_2$ (i.e. more than 50% of $MgH_2$ is formed after 5 h). It is related to the higher mechanical properties of oxides (Young modulus especially) which leads to a higher efficiency of ball milling and then, as reported in Table 1, the median diameter (i.e. $d_{0.5}$) of Mg-oxide mixtures is always lower than that of Mg-metallic mixtures.

No chemical reaction has been observed between magnesium and additive during RMG but for YNi addition, YNi is decomposed into Ni clusters and yttrium hydride (i.e. $YH_2$ and $YH_3$). Such decomposition also occurs as the intermetallic is exposed to hydrogen gas [9]. For oxide additions (and in contradiction with the Ellingham diagram) no reduction of the oxide during the mechanical process seems to occur. The EPMA analysis confirms our hypothesis.

### *3.2. Hydriding properties*

The results concerning the absorption properties of all the studied mixtures are reported in Figs. 1–3 and 5. The case of Co addition has been widely studied and the improvement in the absorption behavior can be attributed to the catalytic effect of Co on the $H_2$ dissociation reaction [7,10]. The most important factor is therefore the complete dispersion of Co in the magnesium matrix.

In the case of YNi addition, the situation is slightly more complicated as YNi absorbs hydrogen during RMG and starts to decompose into yttrium hydrides and nickel [9]. The initial kinetics (Fig. 1) are somehow better than that of Mg+10wt.%Co mixtures but as the mixture contains more additive (i.e. 25wt.% leads to the best sorption kinetics), the maximum quantity of hydrogen absorbed is smaller. However, it is worth noting that the kinetics obtained are almost as good as those reported by Liang et al. [11] for $MgH_2$+3wt.%Ni which is of nanometre size. The good properties of Mg+YNi mixtures must be related to the coupling of two effects: catalysis of Ni cluster and the presence of 'in situ getter' (i.e. $YH_2$ and/or $YH_3$). So, even if the specific surface area of the present studied mixtures (from 0.8 to 3 $m^2/g$) is 10 times lower that that of nanocrystalline Mg+3wt.%Ni, the properties are almost the same.

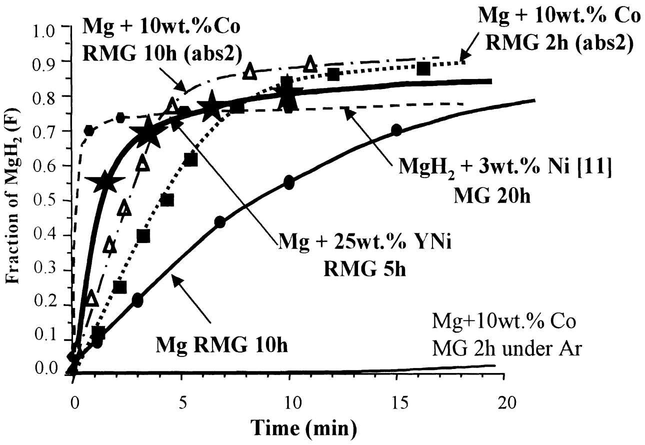

Fig. 1. Hydrogen absorption behavior at $T=300\,^{\circ}\mathrm{C}$ and $P=1.1$ MPa of various Mg-based mixtures containing 10wt% additive (except for YNi where the content is 25wt.%).

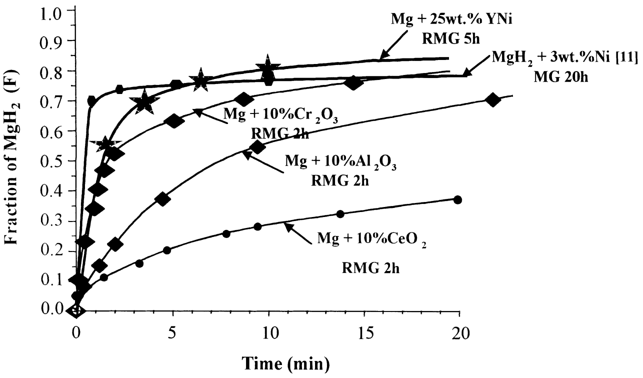

Fig. 2. Hydrogen absorption behavior at $T=300\,^{\circ}\mathrm{C}$ and $P=1.1$ MPa of several Mg+oxide mixtures compared with Mg+YNi and $Mg_{nano}$+Ni [11].

Table 1

Median diameter measured on Mg-oxide and Mg-metallic mixtures ball milled for 2 h

| | Mixtures Mg+10 wt.% of | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $Cr_2O_3$ | $Al_2O_3$ | $Yb_2O_3$ | Co | Ni | YNi | BN | $Cr_2O_3$ FSC[a] |
| $d_{0.5}$ (μm) | 27 | 32 | 33 | 47 | 45 | 54 | 34 | 28 |

The uncertainties are around 5% of the $d_{0.5}$ values.

[a] Only 5 wt.% of $Cr_2O_3$ FSC added.

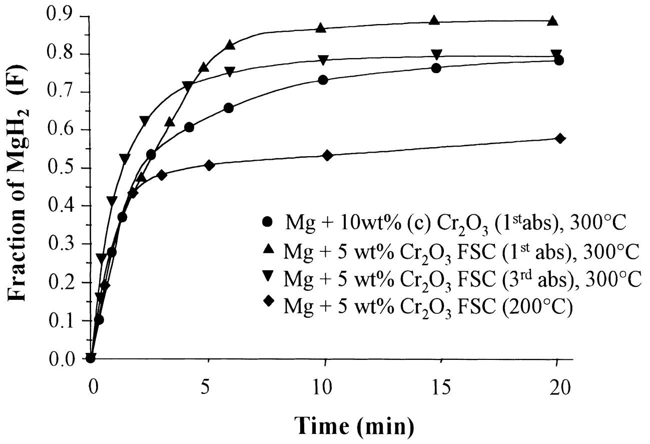

Fig. 3. Hydrogen absorption behaviour at mostly $T=300$ °C and $P=1.1$ MPa of Mg+crystalline $Cr_2O_3$ and Mg+$Cr_2O_3$ FSC.

In the case of oxide additions (Figs. 2 and 3), the improvement of sorption properties depends a lot on the added oxide. Only the oxides of an element that can have different valences exhibit a catalytic effect. The use of a wide variety of oxides (i.e. $Fe_2O_3$, $Fe_3O_4$, $Yb_2O_3$, $TiO_2$, $V_2O_5$, etc.) has confirmed these phenomena [12]. Before the dissociation of $H_2$ molecules, hydrogen has to be adsorbed at the surface of the catalyst and, according to Henrich et al. [13] perfect single crystal oxide surfaces (e.g. $TiO_2$) are completely inert towards reaction with hydrogen. However, hydrogen can be adsorbed at the oxide surface if it contains a higher density of defects (both structural and electronic). Then, the introduction of defects by ball milling explains the rapid absorption kinetics of Mg-oxides. Moreover, the existence of various valence states also implies a source of electronic disorder and therefore, this should also lead to an increase in the hydrogen sorption behaviour. These results are consistent with the earlier work of Oelerich et al. [14].

The use of nanocrystalline materials leads to an improvement of the sorption properties and then, the use of a nanocrystalline additive (i.e. $Cr_2O_3$ FSC) can be interesting too. The use of crystalline $Cr_2O_3$ (i.e. (c)$Cr_2O_3$) leads to the formation of finer particles (Fig. 4). It indicates that the $Cr_2O_3$ FSC should be less brittle than the (c)$Cr_2O_3$ which influences the efficiency of milling. After hydrogenation, both mixtures (i.e. containing (c)$Cr_2O_3$ and $Cr_2O_3$ FSC) exhibit the same particles size repartition. However, it is worth pointing out that the span (i.e. $(d_{0.9}-d_{0.1})/d_{0.5}$) is weaker for the mixture containing $Cr_2O_3$ FSC. The reaction of Mg with hydrogen is controlled by: (i) nucleation and (ii) diffusion of hydrogen through a growing magnesium hydride layer. Therefore, the specific surface area, the particle size and the crystallite size should play a major role. For Mg+$Cr_2O_3$ FSC mixture, the variation of this last parameter as a function of the grinding time is reported in Table 2. The crystallites size of Mg is not very sensitive to either the grinding duration or the hydriding process. In contrast, the crystallite size of $MgH_2$ decreases by a factor of two when the grinding duration increases from 2 to 5 h. As both the crystallite size of $MgH_2$ and the particle size of the mixture decreases, the number of crystallites per particle will be almost constant. Then, the density of the grain boundary is almost constant too so that the kinetics of reaction with hydrogen should be almost the same whatever the grinding duration.

Comparing the sorption properties of Mg+(c)$Cr_2O_3$ and Mg+$Cr_2O_3$ FSC ball milled for 2 h (Fig. 3), no difference in the initial reaction rate can be detected. However, a divergence appears after 2 min and the maximum hydrogen sorption capacity was higher and was reached more

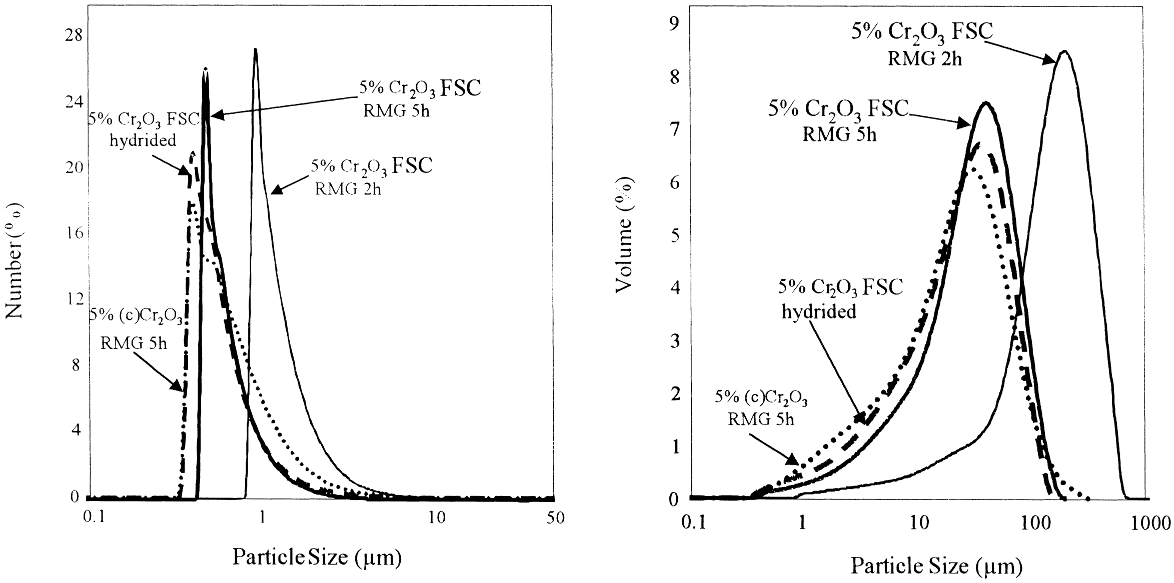

Fig. 4. Results of the particle size measurement. Repartition as a function of number on the left and as a function of volume on the right.

Table 2
Crystallite size of both Mg and $MgH_2$ for different grinding duration and after hydriding at 300 °C for 2 h

| | RMG duration | | | | Hydrided for 2 h at 300 °C |
|---|---|---|---|---|---|
| | 2 h | 3 h | 4 h | 5 h | |
| *L* Mg (nm) | 21.2 (1.6) | 20.6 (1.4) | 22.0 (2.7) | 22.9 (1.0) | 24.0 (2.7) |
| *L* $MgH_2$ (nm) | 20.2 (1.8) | 15.0 (8.7) | 12.9 (0.6) | 11.4 (1.1) | 19.9 (2.0) |

rapidly for the mixture containing $Cr_2O_3$ FSC. As mentioned previously, the number of crystallites per particle is higher for the mixture containing $Cr_2O_3$ FSC and then, the limiting diffusion layer ($MgH_2$ layer on the surface of Mg particle) was reached more slowly. Moreover, the zeta potential of the (Mg+(c)$Cr_2O_3$) mixture is higher than that of (Mg+$Cr_2O_3$ FSC) (i.e. +35 and +22 mV, respectively). As the zeta potential is mainly due to the $Cr^{3+}$ ion on the surface of Mg particle, this difference can be explained by the presence of some Cr atoms (replacing $Cr^{3+}$). The presence of chromium metal can play a major role in the improvement of the sorption properties. Some XPS experiments are in progress to confirm the zeta potential measurements.

After hydridation, the crystallite size of $MgH_2$ increases (Table 2) and the particle size only slightly decreases (Fig. 4) so that the density of the grain boundary decreases. This leads to a decrease in the initial hydriding rate as a function of the number of hydriding/dehydriding cycles. The decrease in the number of nucleation sites by sintering can also be considered. Finally, the absorption properties reported here are very close to that obtained by Oelerich et al. [14] for nanocomposite $MgH_2/Cr_2O_3$ mixtures. Moreover, a significant absorption is obtained at temperatures as low as 200 °C (i.e. almost 3 wt.% after only 1 min).

In Fig. 5, the effects of BN addition are compared with that of graphite addition published by Bouaricha et al. [15]. The large improvement in the absorption properties of (Mg+10wt.% BN) mixture compared with pure magnesium can be related (as it was for graphite addition) to the adsorption of BN layers at freshly exposed magnesium surfaces and the reaction with oxygen species of active B and N radicals formed as a result of B–N bond breaking during the milling operation. Then, the impermeable surface oxide or hydroxide layer is not re-formed and the metallic Mg surfaces are readily accessible to hydrogen. Then the different behaviour between BN and graphite addition can be explained by the difference in structure (existence of stronger interlayer bond in BN compared with graphite) and the difference in oxidation sensitivity [16]. A more detailed study on (Mg+BN) mixtures is under way.

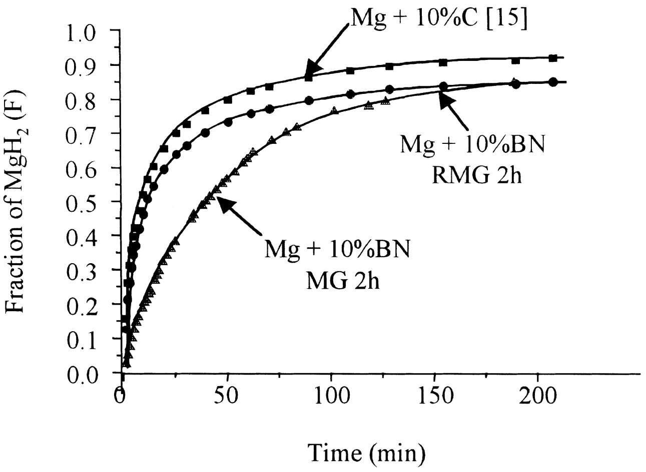

Fig. 5. Hydrogen absorption behaviour at $T$=300 °C and $P$=1.1 MPa of Mg+BN compared with Mg+graphite [15] mixtures.

## 4. Conclusion

RMG is a good way to produce $MgH_2$ 'in situ' and to increase significantly the reactive surface area. Both steps of the hydrogen reaction (i.e. nucleation and diffusion) are improved because of both the creation of defects and the decrease in the number of crystallites per particle for diffusion. Various additives such as oxides, intermetallics and metals have been tried. All additives allow one to improve the sorption properties. Furthermore, for YNi, the decomposition, during RMG, into yttrium hydride and Ni induces: (i) the use of higher wt.% of YNi in the starting mixture and (ii) the best sorption properties. Oxide addition is also effective and the electronic nature of the metal constituent of the oxide appears to be of prime importance. Finally, the sorption properties obtained are very similar to those of nanocrystalline products which offers some promise for the future use of the RMG process.

The results obtained using $Cr_2O_3$ FSC are almost equivalent to those obtained for nanocomposite $MgH_2$/$Cr_2O_3$. The variation of the number of crystallites per particle gives a satisfactory explanation of the phenomenon. These results encourage us to continue this study and to use more widely the supercritical fluid process.

Finally, BN addition has similar effect to graphite addition. The difference in hydrogen sorption property improvement can be correlated with the difference in oxidation behaviour and chemical bonding between C and BN.

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