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# Hydrogen sorption of Mg-based mixtures elaborated by reactive mechanical grinding

J-L. Bobet<sup>a</sup>,\*, B. Chevalier<sup>a</sup>, M.Y. Song<sup>b</sup>, B. Darriet<sup>a</sup>, J. Etourneau<sup>a</sup>

<sup>a</sup>Institut de Chimie de la Matière Condensée de Bordeaux, ICMCB, CNRS [UPR 9048], Université Bordeaux 1, 87. Avenue du Dr A. Schweitzer, 33608 Pessac, Cedex, France

<sup>b</sup>Division of Advanced Materials Engineering, Chonbuk National University, 664-14 1ga Deogjindong Deogjingu, Chonju, 561-756, South Korea

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#### Abstract

The use of mechanical grinding (MG) under  $H_2$  of magnesium powder improves the hydrogen sorption properties. The hydrogenation of Mg starts in situ during the milling process that allows suppressing the activation procedure generally requested for Mg. The effects of the addition of various elements or compounds have been studied. The hydriding is a two-step process: nucleation and diffusion. A direct relationship exists between the nucleation duration and the specific surface. A critical milling time exists below which the diffusion process is improved and above which no further improvement is observed (the maximum internal stress in the powder is also reached at this critical time). The diffusion is controlled by the number of crystallites per particle that can be reduced by increasing the milling time up to 10 h. The addition of Co (catalyst), YNi (hydrogen pump) or oxides (abrasive element and nucleation centre) leads to an improvement of the hydrogen sorption properties (but a strong dependence upon the milling time is reported). Finally, the sorption properties of our mixtures are comparable with thus reported for MgH<sub>2</sub>-metal mixtures. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen absorbing materials; Alloys; Mechanical alloying; Kinetics

# 1. Introduction

Mg is one of the most promising candidates for hydrogen storage materials but its practical application is limited because of the slow hydrogen sorption kinetics and the high dissociation temperature of the hydride [1,2]. One way to overcome these drawbacks is the addition to Mg of some metals or alloys [3–6] by the use of high-energy ball milling (mechanical alloying [7]). More recently, it has been reported that mechanical grinding in a reactive atmosphere allows promotion of the solid–gas reaction. This allows the direct synthesis, at room temperature of nitrides, oxides and hydrides [8].

Various additives have been selected in order to reach the highest hydrogen sorption properties. The catalytic properties of Co should allow a higher dissociation of  $H_2$ into 2H<sup>'</sup>. In the case of YNi (or YNi<sub>2</sub>) addition, this compound should act as a hydrogen pump (YNi absorbs

\*Corresponding author. Tel.: +33-5-5684-2653; fax: +33-5-5684-2480.

hydrogen easily at room temperature and exhibits an equilibrium pressure below  $10^{-5}$  MPa). Finally, the oxides should act as an abrasive element and then improve the efficiency of the milling process. The aim of this study was to reach a better understanding of the influence of reactive mechanical grinding (RMG) and various additions on both the crystallographic and the hydrogen sorption behaviour of Mg+additive mixtures.

# 2. Experimental

YNi and YNi<sub>2</sub> compounds were prepared by melting the constituent elements under a purified argon atmosphere. Homogeneity was achieved by annealing under vacuum at 1073 K for 1 week. The electron microprobe analysis (EMPA) reveals a perfect chemical homogeneity. Then, the samples were crushed and sieved under 100  $\mu$ m.

Pure Mg powder was mixed with additives (initial particle size of 50  $\mu$ m for Mg and 3–7  $\mu$ m, 100  $\mu$ m and 50–150  $\mu$ m for Co, YNi and oxides, respectively, total weight=8 g) in a stainless steel container (with 17

E-mail address: bobet@icmcb.u-bordeaux.fr (J-L. Bobet).

hardened steel balls, total weight=72 g) closed in a hermetic way. All the handlings were performed in a glove box under Ar in order to prevent oxidation. The mill container was then evacuated to a primary vacuum ( $10^{-3}$ MPa) prior to filling with high purity hydrogen gas ( $\approx 1.1$ MPa). The disc rotation speed was fixed to 200 rpm for all the experiments. The experimental procedure, repeated until the total milling time is reached, was as follow: 15 min of milling, 5 min of rest, 15 min of milling, refilling with H<sub>2</sub> gas (1.1 MPa).

The crystalline structure of as-milled powders was characterized by X-ray diffraction (XRD) analysis (10 s/2 $\theta$  step of 0.02°) on a Philips PW 1050 diffractometer using Bragg–Brentano geometry (CuK $\alpha$  radiation). The diffraction patterns were analyzed by a whole pattern fitting procedure (with the Thomson–Cox–Hastings function) using the program FULLPROF [9] in order to determine the lattice parameters, the weight concentration of each phase and both the crystallite size and the internal strain. It is important to notice here that according to the small difference in absorption coefficient, no corrections from it have been carried out ( $\mu_{Mg}$ =6.83·10<sup>-3</sup> µm<sup>-1</sup> and  $\mu_{MgH_2}$ = 5.49·10<sup>-3</sup> µm<sup>-1</sup>).

The granulometric study was done using a Malvern 2000 instrument (based on Laser diffusion scattering). The measurement were done in a liquid medium (ethanol). The hydriding apparatus has been described previously [10].

# 3. Results and discussion

#### 3.1. Structural and chemical study

It has already been shown that RMG of Mg based mixtures results in the partial formation of MgH<sub>2</sub> [11]. The amount of MgH<sub>2</sub> formed as a function of milling time is estimated using Rietveld refinement of XRD patterns as well as by thermogravimetric measurements. The results concerning most of the studied mixtures are reported in Fig. 1. The diffraction patterns did not reveal any change in the lattice parameters indicating that, as expected (i) almost no solid solution of H in Mg exists and (ii) the stoichiometry H:Mg for MgH<sub>2</sub> is strictly equal to 2. Fig. 1 reveals that whatever the metallic compounds or intermetallic used, the trend observed for the formation of MgH<sub>2</sub> is the same (i.e. about 10% of MgH<sub>2</sub> formed after 2 h and around 30-40% after 5 h). However, it also clearly appears that the addition of oxides (CeO<sub>2</sub> and  $Cr_2O_3$ ) strongly increases the transformation of Mg into MgH<sub>2</sub> (i.e. more than 50% of  $MgH_2$  is formed after 5 h). Such different behaviour was expected because of the mechanical properties of oxides compared with that of metallic element or intermetallic. For example, the Young modulus of  $Cr_2O_3$  which is comparable with that of the other oxides studied here, is five times higher than that of the metallic elements Co or Ni. As a resume on the mechanical



Fig. 1. Fraction of  $MgH_2$  formed as a function of milling time for different Mg based mixtures.

properties we can conclude that the oxides have a brittle behaviour as the metals exhibit a much more ductile behaviour. Then, the efficiency of ball milling is higher and the energy transferred to the powder is higher too. The granulometric measurements reported in Table 1 provide new proof of the higher efficiency of grinding as the median diameter  $(d_{0.5})$  of Mg–Cr<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> mixtures is always lower than that of Mg–metallic mixtures.

However, we also report in Table 1 a singular behaviour for Mg+10 wt.% CeO<sub>2</sub>. The SEM observations reveal the presence of large agglomerates in the powder for this mixture. This has been attributed to the strong hygroscopy of CeO<sub>2</sub>. Some experiments using calcinated CeO<sub>2</sub> are underway to clarify this expected result.

From Fig. 1, it appears that Mg is still present even for long periods of RMG (up to 20 h). The formation of  $MgH_2$  seems to be rapid during the first 10 h but slow thereafter.

We also notice in the XRD patterns that the peaks related to  $MgH_2$  are broader than those of Mg indicating a difference in the size of the crystallites. The crystallite size of Mg is around 30 nm and that of  $MgH_2$  is around 15 nm. The explanation comes again from the mechanical properties of  $MgH_2$  and Mg. The hydride can be considered as a brittle material as pure Mg is well known to have a ductile behaviour. Then, the ball milling is more efficient in the case of  $MgH_2$  compared with that of Mg. Moreover the hydride is formed from Mg which is more and more amorphous (smaller crystallites size). Fig. 2 shows the crystallite size of Mg and internal strain as a function of milling time. The larger reduction of the crystallite size

Table 1

Median diameter measured on Mg–oxide and Mg–metallic mixtures ball milled for 2 h. The uncertainties are around 5% of the  $d_{0.5}$  values

Mixtures Mg+10 wt.%	Cr <sub>2</sub> O <sub>3</sub>	$Al_2O_3$	CeO <sub>2</sub>	Co	Ni	YNi
d <sub>0.5</sub> (μm)	27	32	153	47	45	54



Fig. 2. Evolution of the crystallites size (L) and the internal strain  $(\mu\sigma)$  as a function of milling time.

during MG (under argon) compared with RMG can also be linked with the mechanical properties. However, the formation of  $MgH_2$  (which is exothermic) during RMG provides some 'thermal' energy that increases the crystallite size.

For RMG experiments, we notice that increasing the milling duration beyond 10 h does not lead to significant changes in the crystallite size of either Mg or MgH<sub>2</sub>. As we already notice the same phenomenon in the MgH<sub>2</sub> formation, we conclude that the efficiency of grinding beyond 10 h is low. The process of the MgH<sub>2</sub> formation could be assumed to be firstly the adsorption of hydrogen on particles created by crushing (fresh surface) and then diffusion of the adsorbed hydrogen into the metals to form metal hydrides. On the basis that the milling efficiency beyond 10 h is low, no fresh surfaces would be created and the formation of MgH<sub>2</sub> would be considerably reduced.

The partition of additive in the Mg matrix is also important for the hydrogen sorption characteristics. The results of EMPA reveals that a milling time of 2 or 3 h allows an almost random dispersion to be obtained. The minimum grinding time for a complete dispersion is obtained for oxide addition and the maximum time is obtained for the YNi addition. Once again it can be explained in terms of the mechanical properties of the additives and then in terms of ball milling efficiency.

Finally, we investigated the occurrence of chemical reaction between magnesium and additive during RMG. For metallic elements additions no ternary hydrides such as  $Mg_2CoH_5$  were formed. For YNi addition, it has been observed that the YNi additive is decomposed into Ni clusters and yttrium hydride (i.e.  $YH_2$  or  $YH_3$ ). Such a decomposition occurs as the intermetallic is exposed to hydrogen gas as reported elsewhere [12]. For oxide additions, the Ellingham diagram suggested that in the temperature range of mechanical alloying (i.e. up to 500°C as reported for a shock), and though MgO is more stable than  $Cr_2O_3$ ,  $Al_2O_3$  and  $CeO_2$  (per mol oxygen), the three oxides are not reduced during the mechanical process. The EMPA analysis confirms our hypothesis.

# 3.2. Hydriding properties

The different Mg-based mixtures were ball milled for 2 h under a hydrogen atmosphere. In the case of Mg–Co mixtures, we already published [13] a hypothesis on the mechanism of the absorption phenomenon. It consists of two steps: a nucleation process followed by a diffusion process. The first step of the reaction is controlled by the surface and so, ball milling under hydrogen allows a significant improvement. The second step of the process is controlled by the number of crystallites per particles. To a first approximation, we could conclude that the driving force of diffusion in the case of MG product is the intragrain diffusion as shown by Zaluska et al. [14] as in the case of RMG product, the intergrain diffusion should not be considered as negligible.

Fig. 3 shows the kinetics behaviour of various magnesium based mixtures containing 25 wt.% of additive. It appears that whatever the additive element or compound used, almost the same results in terms of kinetics were obtained. Hence, all these results did not reveal many trends about the additive effect. We then studied the hydrogen sorption on some mixtures containing less additive. Except for YNi addition, the best results were obtained for mixtures containing <10 wt.% additive (Figs. 4 and 5).

Whatever the additive is, the diffusion is improved by increasing the milling time up to 10 h as expected from the creation of defects. Beyond 10 h, the milling, reported to be almost ineffective (no more internal stress generated), does not lead to any improvement. RMG allows to increase the specific surface and then, to improve widely the sorption properties of all the studied mixtures.

Moreover, for all the additives (except YNi), no significant variation of the diffusion coefficient (defined in [13,15] as  $C = D_{\rm H} k (P_0^{1/2} - P_{\rm eq}^{1/2})$  has been observed. In the case of Co addition, the improvement of the absorption



Fig. 3. Hydrogen absorption behaviour of various Mg based mixtures containing 25wt.% additive (triangle=MmNi<sub>5</sub> addition [5], open circles=LaNi<sub>5</sub> [5], black star=YNi [12], bold circle= $Y_{1-x}Ni_2$  [12] and bold square=Co [11]).



Fig. 4. Hydrogen absorption behaviour at  $T=300^{\circ}$ C and P=1.1 MPa of various Mg based mixtures containing 10wt.% additive (except for YNi where the content is 25wt.%). All are our work except MgH<sub>2</sub>+3wt.% Ni which was done by Liang et al. [21].

behaviour can be attributed to the catalytic effect of Co on the  $H_2$  dissociation reaction as reported elsewhere [16–18]. The most important factor is the complete dispersion of Co in the magnesium matrix.

In the case of oxide additions (Fig. 5), it appears that the improvement of sorption properties depends much on the added oxide. Only the oxides of an element which can have different valences and hence can adopt different electronic states, have a catalytic effect. For catalysis, the local electronic structure of the catalysts is of great importance; before the dissociation of H<sub>2</sub> molecules, the hydrogen has to be adsorbed at the surface of the catalyst. However, according to Henrich et al. [19] perfect single crystal oxide surfaces (e.g.  $TiO_2$ ) are completely inert towards hydrogen. However, they also reported that H<sub>2</sub> can be absorbed at the oxide surface if it contains a higher density of defects (both structural and electronic). Then, as ball milling introduced some structural defects (as reported previously as internal stress), it could explain the fast absorption kinetics of Mg-oxides. Moreover, the existence



Fig. 5. Hydrogen absorption behaviour at  $T=300^{\circ}$ C at P=1.1 MPa of various Mg based mixtures containing 10wt.% additive (except for YNi where the content is 25wt.%). All are our work except MgH<sub>2</sub> + 3wt.% Ni which was done by Liang et al. [21].

of various valence state is also a source of electronic disorder and then, this should also lead to an increase of the hydrogen sorption behaviour (e.g. Cr<sub>2</sub>O<sub>3</sub>). Previous work by Oelerich et al. [20], confirms our hypothesis. The case of CeO<sub>2</sub> addition is somewhere atypical. We were expecting almost the same behaviour as for  $Cr_2O_3$  addition but we obtained somewhat even lower kinetics than in the case of Al<sub>2</sub>O<sub>3</sub> addition. The explanation comes probably from the chemical nature of CeO<sub>2</sub>. As shown in Table 1, the median diameter of Mg-CeO2 mixture is five times higher than that obtained for the other Mg-oxide mixtures. As the mechanical properties of  $CeO_2$  are close to those of the other oxide, we must conclude that the strong affinity of CeO<sub>2</sub> towards water is probably responsible of the agglomeration of particles inducing a lower specific surface which leads to poor hydrogen sorption behaviour. The calcination of CeO<sub>2</sub> prior the mixture would probably lead to an improvement of the sorption properties.

The case of YNi addition is a little more complicated as YNi absorbs hydrogen at room temperature and normal pressure [12]. So, during RMG, YNi absorbs hydrogen and starts to decompose into yttrium hydrides and nickel. The nickel is well known to have a strong catalytic effect on the H<sub>2</sub> dissociation reaction and so we expected at least the same sorption property improvements as those reported for Co addition. As shown in Figs. 4 and 5, the initial kinetics is somewhat better than that of the Mg+10wt.%Co mixtures but as the mixture contains more additive (25wt.%), the maximum quantity of hydrogen absorbed is smaller. However, the kinetics obtained are almost as good as those reported by Liang et al. [21] on MgH<sub>2</sub>+3wt.%Ni which is of a nanometric size. The good properties of the Mg+YNi mixture must be related to the coupling of two effects: catalysis of Ni cluster and presence of 'in situ getter' (i.e. YH<sub>2</sub> and/or YH<sub>3</sub>). So, even if the specific surface of our mixtures (from 0.8 to  $3 \text{ m}^2/\text{g}$ ) is ten times lower that that of nanocrystalline Mg+3wt.%Ni the properties are almost the same.

The desorption behaviour has not been extensively studied yet. In Fig. 6, we reported the preliminary results of desorption kinetics. Under the same conditions, the desorption of pure magnesium is very slow (0.4 wt.% desorbed in 30 min at 310°C) [23]. Once again the Mg–YNi mixture behaves in a different manner. The best desorption kinetics are obtained for the mixture containing 25% of YNi as for the other mixture the optimum additive content is below 10wt.%.

The Mg–oxide mixtures exhibit relatively poor kinetics compared to those of the Mg–Co mixtures. The same trend as already reported for absorption behaviour is observed. Even if our mixtures are not nanocrystalline, the desorption kinetics are comparable to those of nanocrystalline materials [22] showing that the Co addition is effective for the improvement of both absorption and desorption. However, the best kinetics are obtained in the case of the MgH<sub>2</sub>+V mixture [21] which proves the great importance



Fig. 6. Hydrogen desorption behaviour of various Mg based mixtures containing 10wt.% additive (except for YNi where the content is 25wt.%). All are our work except MgH<sub>2</sub> + 10% V which was done by Liang et al. [21].

of the starting product. Finally, it is important to note that RMG process applied to the Mg–Co mixture allows a non negligible desorption at low temperature (i.e. 1.3 wt.% in 30 min at 200°C and almost 1 wt.% in 1 h at 100°C).

### 4. Conclusions

We report in this paper that RMG is a good way to produce 'in situ' magnesium dihydride. Such a process allows to increase significantly the reactive surface (increase of the specific surface). Both steps of the hydrogen reaction (i.e. nucleation and diffusion) are improved by increasing milling time up to 10 h because of both the creation of defects and the decrease of the number of crystallites per particle for diffusion. However, the improvement is higher during the first 5 h. Finally, beyond 10 h of milling no further improvement is reported because no additional defects are created. Under our conditions, 10 h is assumed to be a critical time beyond which milling is not efficient.

Various additives such as oxides, intermetallics and metals have been tried. All additives improve the sorption properties. However, in the case of YNi, the decomposition, during RMG, into yttrium hydride and Ni requires the use of higher wt.% of YNi in the starting mixture. The oxide addition is more effective for the absorption process than for the desorption one. Moreover, the electronic nature of the metallic constituent of the oxide appear to be of prime importance. Finally, the sorption properties obtained are very close to those of nanocrystalline product which is promising for RMG process.

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