JOURNAL OF Materials CHEMISTRY

Preparation of Mg_2Co alloy by mechanical alloying. Effects of the synthesis conditions on the hydrogenation characteristics†

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Received 6th May 1998, Accepted 29th June 1998

The influence of the synthesis route of Mg_2Co hydrogen-storage alloy has been studied. It is shown here that mechanical alloying (MA) allows one to obtain crystallized products after milling for 100 h. It seems to crystallize in a face centered cubic structure ($a = 1.153$ nm). However, when the milling is continued beyond 100 h the amorphisation of Mg_2Co is observed. After 210 h of milling Mg_2Co is obtained with a yield of about 80%. Furthermore, when the product is annealed, the face centered cubic structure is maintained but the intensity ratio of the diffraction peak is changed markedly. When the milling time increase, the grain and crystallite size decrease so that the rate of the hydruration increases. However, at the same time, a passivation mechanism should occur so that the maximum hydrogen storage capacity decreases.

1 Introduction

Among the hydrogen storage materials, magnesium based alloys are considered to be promising candidates for their high hydrogen storage capacity, light weight, low cost and abundance in the earth's crust.[1] At the beginning of 1980, much interest was focused on Mg_2Ni, which forms a stable hydride, Mg_2NiH_4. This alloy was prepared by a solid–solid reaction under argon atmosphere at 450 °C.[2] Several experiments were done in the same way to prepare Mg_2Co and Mg_2Fe, but these compounds never formed. However, under hydrogen pressure (1.5 to 5 MPa) the mixture $2Mg + Co$ (or $2Mg + Fe$) reacts at high temperature (about 350 °C) to form Mg_2CoH_5 (or Mg_2FeH_6). Some attempts were also made to prepare these alloys by mechanical alloying (MA): Mg_2Ni was easily obtained[3–6] but the formation of Mg_2Co (and Mg_2Fe) was not reported. However, the existence of Mg_2Co, ignored by most authors, was reported by Konstanchuk *et al.*[7,8] (obtained by dehydruration of Mg_2CoH_5).

MA has recently emerged as a novel technique for alloy formation.[9,10] The resulting product can be crystalline, amorphous or quasi-crystalline.[11] Magnesium based alloys have slow hydriding and dehydriding kinetics and the reaction with hydrogen takes place at temperatures higher than 500 K. Since MA by ball milling leads to materials in fine particle form, which may result in reduction of the activation time and of the temperature, this method may be typically suited for the synthesis and formation of the hydrogen storage materials Mg_2M (M = Ni, Co and Fe).

It has been reported[7,8] that the substitution of Ni for Co in Mg_2Ni leads to an improvement of the hydrogen storage properties. In this study, we demonstrate that the MA synthesis process is a suitable method for the preparation of crystalline Mg_2Co and also amorphous Mg_2Co. This method allows one to obtain Mg_2Co with a yield of more than 80%. We also study the influence of ball milling on the hydrogen sorption properties of Mg_2Co. To the best of our knowledge, such a study has never been carried out.

2 Experimental details

MA was carried out with pure elemental powders of Mg and Co (respective particle sizes of 300 and 30 μm). The required stoichiometric atomic ratio of pure metal powders was mixed inside an argon dry box and placed in stainless steel containers which were hermetically sealed with an O-ring. Each container was loaded with 8 g mixed powders and 120 g of stainless steel balls (diameter 10 mm: 90 g; diameter 5 mm: 30 g). MA was performed with a Fritsch pulverisette 5 high energy instrument. This apparatus generates (i) a friction interaction and (ii) a shock interaction. The rotation speed of the plate was 200 rpm and the rotation speed of the vials was fixed at 1.25 times the plate rotation speed.

The structural changes of the MA powders were analyzed by X-ray diffraction using a Philips PW 1050 diffractometer and/or a Siemens D 5000 diffractometer with Cu-Kα radiation ($\lambda = 0.15418$ nm). A numerical method included in the Diffract-At software was used to analyze the XRD patterns and to obtain the positions and the integral width (β) of the diffraction peaks.

For each Bragg peak the integral width (β_{exp}) was determined and the instrument broadening (β_{inst}) measured *versus* a standard (Si and/or LaB_6) was subtracted to obtain β_{sample}:

$$\beta_{sample} = (\beta_{exp}{}^2 - \beta_{inst}{}^2)^{0.5}$$

To a first approximation, the crystallite size (in Å) can be calculated from the Scherrer formula:

$$L = K\lambda/\beta_{sample}\cos\theta$$

where K is a constant depending on both the apparatus and the sample studied ($0.9 < K < 1$), λ is the X-ray wavelength (in Å), β_{sample} is the integral width of the sample (in radians) and θ is the diffraction angle.

However, in the case of ground solids, many studies have shown that the Scherrer equation under-evaluated the crystallite size, and a best estimation of it can be obtained using:

(i) the Williamson and Hall formula

$$\beta_{sample}\cos\theta = K\lambda/L + 4\langle\varepsilon^2\rangle^{1/2}\sin\theta$$

where $\langle\varepsilon^2\rangle$ is the quadratic mean of the internal strain;

(ii) multiple line profile analysis (with software by Ji[12] and Bobet[13] developed the major difference between these two methods and the Scherrer formula is that in (i) and (ii) the internal strain is taken into account. The difference between (i) and (ii) is that the second method allows one to consider directly the anisotropy of both the crystallite size and the internal strain.

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†Basis of the presentation given at Materials Chemistry Discussion No. 1, 24–26 September 1998, ICMCB, University of Bordeaux, France.

The chemical composition and homogeneity of the compounds were checked by electron microprobe analysis with a CAMECA SX-100 instrument. The quantitative determination was performed on the basis of intensity measurements of Mg-Kα_1 and Co-Kα_1 X-ray emission lines using Mg_2Ni, $MgNi_2$ and pure cobalt as reference compounds.

The hydriding apparatus used has been described previously.[14] The sample reactor, while being heated to 400 °C, was evacuated to primary vacuum by a mechanical pump for 1 hour. Hydrogen gas was then introduced into the sample reactor to a pressure of about 0.5 MPa and a temperature ranging from 150–350 °C. Heating was stopped (and the temperature was maintained constant) when absorption started and the pressure was kept constant at 0.5 MPa. The absorbed amount of hydrogen was then recorded every 3 min for 90 min. After that, the sample was heated to 400 °C and a hydrogen gas pressure of about 5 MPa was introduced in order to complete the hydruration.

3 Results and discussion

3.1 Results

MA product characterization. We studied the effects of ball milling on the reactivity of the initial mixture (2Mg+Co). The X-ray diffraction patterns of the products milled several times are shown in Fig. 1 (this crystallographic analysis was performed in air). From 0–210 h of milling, a decrease in the intensity and a broadening of peaks, characteristic of Mg, is observed. This phenomenon is most noticeable during the first 50 h. It is also worth noting the modification in the intensity ratio of the first three peaks ($32° < 2\theta < 37°$) due to the plastic deformation of Mg particles occurring under the grinding effects. The crystallite size M(Mg) (normalized to unity for the starting Mg) decreases monotonously from 0–210 h but the decrease is most marked during the first 50 h of milling as shown in Fig. 2. During the same time, the internal strain σ(Mg) (Fig. 2) reaches its maximum value and when the milling is continued the internal strain does not decrease, so that the milling induced a decrease of the crystallite size. It is also important to note that after annealing at 450 °C for 8 days, the strain is almost all relaxed and the crystallite size M(Mg annealed) increases a little but does not reach the initial value. This fact clearly indicates that ball milling has definitively changed the microstructure of the product. The decrease in intensity of the magnesium lines has also to be correlated to the fact that there is less and less magnesium metal in the mixture as indicated in Table 1. The quantity of magnesium metal in the mixture was estimated by image analyses of (i) secondary electron and (ii) optical microscopy images.

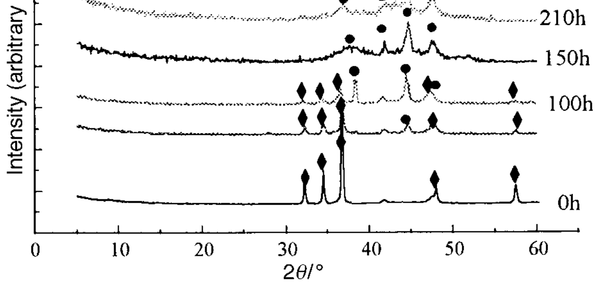


Fig. 1 X-Ray diffraction patterns of the initial composition (2Mg+Co) for different milling times.

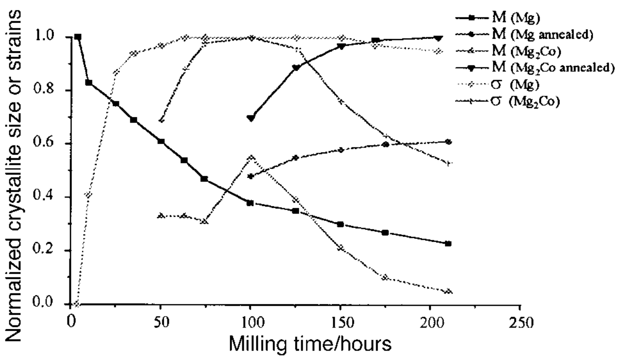


Fig. 2 Evolution of the crystallite sizes (M) and of the internal strains (σ) as a function of milling time.

Table 1 Magnesium metal content (atom%) in the mixture as a function of milling time

	Mg content/atom%	
Milling time/h	Secondary electron pattern	Optical microscopy image
0	69(4)	65(3)
35	59(4)	58(3)
50	49(3)	45(3)
100	18(3)	19(2)
210	12(3)	13(2)

These results show that the quantity of magnesium metal in the milled products decreases slightly from 0–50 h and after that decreases strongly. This suggests that a new phase containing magnesium has been formed after 50 h of milling. It should also be pointed out that when the milling is continued up to 210 h, the quantity of magnesium metal remains almost constant.

In Fig. 1, some new Bragg peaks appeared in the diffraction patterns after about 50 h of milling correspond to Mg_2Co phase. These new peaks increase in intensity until 100 h. As shown in Fig. 2, the crystallite size $M(Mg_2Co)$ of this new compound reaches its maximum value after 100 h and then decreases. This non-monotonous evolution can be directly correlated to the evolution of internal strain $\sigma(Mg_2Co)$. As a matter of fact, the strain is at a maximum after 100 h of milling and then decreases by about a factor of two. This relaxation of strains leads to a decrease of the crystallite size. When milling is continued beyond 100 h, the crystallite size decreases and amorphisation of the new product begins.

The electron microprobe analysis (Table 2) gives the composition of the new products: Mg_2Co (phase 1) two solid solutions; exists alongside $Mg_{1-x}Co_x$ with $x=0.05$ (phase 2) and $Co_{1-y}Mg_y$ with $y=0.03$ (phase 3).

The existence of Mg_2Co has already been mentioned by two groups,[7,8] but it was obtained by dehydruration of Mg_2CoH_5. The first group assumed a face centered cubic structure while the second assumed an orthorhombic structure. Therefore, the X-ray diffraction peaks of our products can be indexed with face centered cubic symmetry ($a \approx 1.14$ nm). However, even if the face centered cubic structure can be retained in our case, the intensity of each peak does not fit exactly and some peaks such as (111) ($2\theta \approx 13.4°$) are missing in the diffraction pattern. For this reason it is not possible to establish the validity of the cubic centered structure type. As for Mg metal, this modification in the intensity ratio should be due to the plastic deformation of Mg_2Co particles occurring during milling.

After annealing at 450 °C for 8 days under vacuum, some additional diffraction peaks (Fig. 3) appeared and the intensity ratio was modified again. (111) ($2\theta \approx 13.4°$) and also (333) ($2\theta \approx 41.1°$) peaks appear and the intensities of some others increase suggesting that the preferred orientation induced by

Table 2 Results of electron microprobe analysis for different synthesis conditions

	Phase 1, Mg_2Co		Phase 2, $Mg_{1-x}Co_x$		Phase 3, $Co_{1-y}Mg_y$	
	Mg (atom%)	Co (atom%)	Mg (atom%)	Co (atom%)	Mg (atom%)	Co (atom%)
Milled 100 h	66 (3)	34 (2)	95.4 (2.1)	4.6 (0.4)	2.5 (0.5)	97.5 (1.6)
Milled 210 h	66 (3)	34 (2)	95.2 (2.0)	4.8 (0.5)	3.1 (0.5)	96.9 (1.5)
Milled 150 h + annealed at 450 °C	67 (3)	33 (2)	94.6 (2.1)	5.4 (0.5)	3.4 (0.5)	96.6 (1.5)

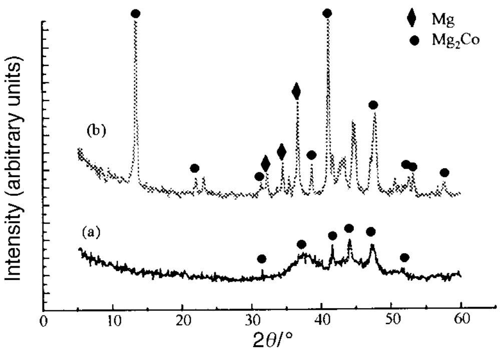


Fig. 3 X-Ray diffraction patterns of the initial composition (2Mg+Co) milled for 150 h: (a) without thermal treatment and (b) annealed at 450 °C for 8 days.

the milling effects disappears during annealing (as suggested by the relaxation of strain caused by annealing). Whatever the milling time, annealing induces an increase of crystallite size and a new intensity ratio for both Mg and Mg_2Co. However, the changes in the diffraction patterns could also be attributed to a modification in the structure of Mg_2Co during annealing. In order to clarify this point, some electron diffraction experiments are under way.

The product milled for 210 h was submitted to differential thermal analysis (Fig. 4). Two exothermic peak were observed (at about 130 and 350 °C) and correspond to the crystallization Mg and of Mg_2Co respectively. It is interesting to note that the area of the first peak decreases with increasing milling time (because the Mg metal content decreases, as shown in Table 1), while the area of the second one increases with increasing milling time (because the Mg_2Co content increases and is less and less crystallized).

3.2 Discussion

From all the previous observations mentioned, we can assume the following reaction path (c stands for crystalline, and am stands for amorphous): (i) from 0–100 h of ball milling, the X-ray diffraction study as well as the electron microprobe analysis clearly highlight the appearance (formation) of a new crystalline compound: Mg_2Co. At the same time, a solid solution of magnesium $Mg_{1-x}Co_x$ (observed to be almost amorphous by X-ray diffraction) and a solid solution of cobalt $Co_{1-y}Mg_y$ (which is not much amorphized as revealed by an X-ray diffraction study carried out using Cr-Kα radiation) are also formed; (ii) beyond 100 h of ball milling (and up to at least 210 h) there is an amorphisation of the Mg_2Co compound; (iii) after annealing at 130 °C, the solid solution of magnesium crystallized (as revealed by DTA) and the other products are not modified; (iv) after annealing at 350 °C, the amorphous Mg_2Co compounds crystallized (as revealed by DTA).

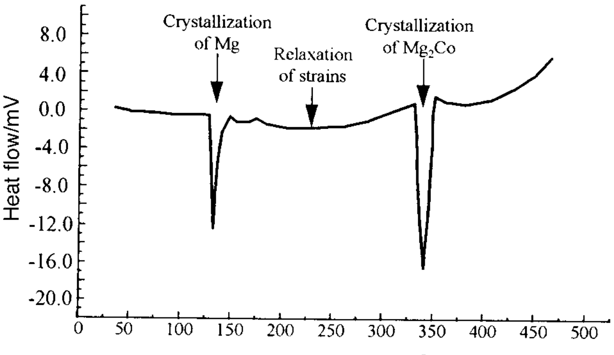
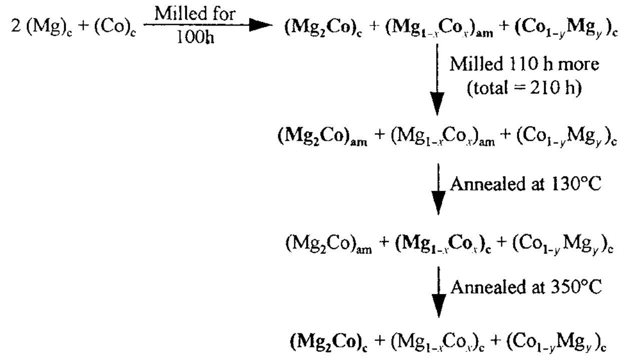


Fig. 4 Profiles of differential thermal analysis of the mechanically alloyed Mg_2Co with a milling time of 150 h.



Scheme 1

The reaction path can be summarized as shown in Scheme 1.

Hydrogen sorption properties. A few studies[15,16] have already been performed on the hydrogen storage properties of Mg_2Co compounds. When a mixture of 2Mg+Co is heated under hydrogen pressure, the stable hydride obtained is Mg_2CoH_5 (space group $Fm\bar{3}m$, $a = 0.6453$ nm).

In Table 3, we report the maximum number of hydrogen atoms per formula unit (n_H) which are absorbed after completion of hydruration ($T = 450$ °C and $P = 5$ MPa for at least 1 h). To gain information about the kinetics of the formation of the products obtained by mechanical alloying with hydrogen, we also report the values of n_H after 30 and 90 min and the ratio between these values and the maximum n_H value. The X-ray diffraction patterns of all the compounds after hydruration revealed the presence of (i) MgH_2 (structure TiO_2 type) and (ii) Mg_2CoH_5.

The following observations can be made: (i) the maximum

Table 3 Hydrogen sorption properties as a function of process conditions

Process conditions	n_H after 30 min	n_H after 90 min	n_H maximum
Milled 100 h	2.1 (50%)	3.1 (74%)	4.2
Milled 150 h	2.1 (55%)	3.3 (79%)	3.8
Milled 210 h	2.2 (65%)	3.1 (91%)	3.4
Milled 150 h + annealed at 450 °C	2.3 (51%)	3.4 (76%)	4.5
Ref. 15	—	—	5

hydrogen sorption capacity is lower than that observed previously[15] on the solid–solid reaction compounds: the obtained value is about 20% lower than the expected value; (ii) increasing the milling time leads to a decrease of n_H and to an improvement of the kinetic of reaction with hydrogen; (iii) annealing leads to a increase of n_H and to an decrease of the rate of reaction with hydrogen

The rate of reaction with hydruration can be directly correlated to the grain size and the crystallite size. When the grain and crystallite size decrease, the specific area increases so that the adsorption of hydrogen is easier and the rate of reaction with hydrogen increases. However, we also observed that when the milling time increases, the maximum hydrogen sorption capacity decreases. This phenomenon can be explained in the same way. In fact, when the grain and crystallite size are very small, the reactivity *vs.* polluting agent increases and a passivation mechanism can occur.

Moreover, the difference in the maximum absorption capacity between the ball milled product and the annealed product can also be attributed to the change in the structure of Mg_2Co.

Some studies on the dehydruration behavior are under way in order to establish the stability of Mg_2Co compounds.

4 Conclusion

In this study, we demonstrate that the MA process is a suitable route to prepare crystallized or amorphous Mg_2Co compounds. As this compound can not be prepared by the classical route (solid–solid reaction) we can conclude that Mg_2Co is a metastable phase. By annealing, the Mg_2Co structure seems to be modified. Some electron diffraction analyses are under way to confirm the results obtained.

Moreover, the decrease of grain size during milling leads to an increase of the rate of hydruration but also to a decrease of the maximum hydrogen sorption capacity. A study of the dehydruration process is underway.

The authors are indebted to L. Roudier for great technical assistance.

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Paper 8/04971H