Journal of Alloys and Compounds 253–254 (1997) 34–37

Characterization and hydriding properties of Mg-graphite composites prepared by mechanical grinding as new hydrogen storage materials

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Abstract

The characteristics and hydriding properties of novel Mg/G composites as prepared by mechanical grinding (MG) of magnesium metal powder and graphite (G) in the presence of cyclohexane (CH) or tetrahydrofuran (THF) have been studied. The use of graphite led to chemical modifications that improved the hydriding properties of magnesium. The Mg/G composites were more active and effective for hydrogen absorption than reported previously. The additives CH and THF in the MG process influenced strongly the hydriding activity of $(Mg/G)_{CH}$ and $(Mg/G)_{THF}$, respectively. The quantities of CH and THF required for optimal activity of $(Mg/G)_{CH}$ and $(Mg/G)_{THF}$ are quite different. For $(Mg/G)_{THF}$, MG of 1 h and THF of 6.1 cm^3 gave the best results while the formation of good $(Mg/G)_{CH}$ composites required MG of 20 h and the presence of CH of 12 cm^3. The different influence of CH and THF on the characteristics of the Mg/G composites are also discussed. The composites formed upon grinding in the presence of CH or THF contain finely divided magnesium which is in intimate contact with the aromatic carbon of graphite. This leads to synergetic effects which result in the formation of an effective hydrogen-absorbing material.

Keywords: Composites; Hydrogen absorption; Hydrogen storage; Mechanical grinding; Magnesium

1. Introduction

Magnesium and magnesium-based alloys have a considerable potential as rechargeable hydrogen storage materials [1,2]. We have made an endeavor to put them into practical applications by using different techniques [3–9]. In earlier publications [8,9], we have described the characteristics of some novel magnesium/graphite (Mg/G) composites which were prepared by mechanical grinding (MG) of the components. It was shown that graphite modified chemically the Mg/G composites, thus improving their hydriding and dehydriding properties. Organic additives in the MG process of magnesium and graphite such as tetrahydrofuran (THF) played an important role in the formation of Mg/G composites, thus reflecting the characteristics responsible for hydriding and dehydriding [8,9]. To examine further the effects of additives such as cyclohexane (CH) and as THF, we have studied the characteristics of the Mg/G composites and their hydriding properties relative to the preparative conditions.

2. Experimental

2.1. Materials

Magnesium (99.95%; 100 mesh; Rare Metallic Col. Ltd.) and graphite (grade: SP-1; Union Carbide Co) were identical with those used in previous works [8,9]. Cyclohexane (reagent grade, Wako Pure Chemical Ind. Ltd.) was used without further purification. Tetrahydrofuran was of research purity and further purified by distillation in the presence of sodium wire.

2.2. Sample preparation and procedures

The Mg/G composites were prepared in a planetary-type ball mill (High G: BX 254; Kurimoto Ltd., balls: SUS 304; diameter: 4 mm; 238 g), capable of operating under conditions of 150 G. A typical preparation consisted of placing graphite (1.8 g), magnesium powder (4.2 g) and cyclohexane (CH; 0–15 cm^3), in this order in a mill pot (SUS 304; cylindrical shape; volume: 170 cm^3) which was flushed thoroughly with dry nitrogen. The mixtures were subjected to MG under different conditions to yield

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PII S0925-8388(96)03074-5

composites, designated hereafter as $(Mg/G)_{CH}$. Upon completion of grinding, the mill pot was opened to take out the sample in a dry-nitrogen glove bag. All composite samples prepared in this way were handled without exposure to air.

Hydrogen absorption measurements were made using a volumetric glass equipment connected to a high vacuum system (~1.3×10^{-3} Pa). Prior to the measurements the sample was degassed under vacuum at 623 K for 2 h, heated to 453 K and brought in contact with hydrogen at 66.7 kPa. The changes in pressures of hydrogen upon absorption were monitored with a baratron (MKS Instruments Inc.: 127AA-01000B). Carbon monoxide chemisorption was carried out with an ordinary volumetric technique at room temperature, the details of which have been previously described [8,9]. X-ray diffraction (XRD) spectra were recorded on a Shimazu diffractometer (XD-D1) using Cu-K_{α} radiation.

3. Results and discussion

3.1. Effects of additives on hydriding of Mg/G composites

The organic additives in the MG process strongly affected the hydriding characteristics of the resulting Mg/G composites as well as their physicochemical properties such as the structure of the surface and the interface. For the preparation of Mg/G composites, cyclohexane (CH) was mainly examined as an additive, and compared with tetrahydrofuran (THF).

The principal features of composites ground without the additives $(Mg/G)_{none}$ were as follows. According to previous reports ball-grinding techniques of magnesium systems produce fresh active surfaces, which result in increased hydrogen-absorption rates [10–12]. As shown in Fig. 1, however, the hydriding activity of $(Mg/G)_{none}$ (S-1) is very low at 453 K and 66.7 kPa of hydrogen. $(Mg/G)_{none}$ showed yields of only $\alpha=$~0.05 after 20 h of reaction time, where α is the fraction of magnesium reacted with hydrogen. As shown by XRD (Fig. 2) the layer structure of graphite (see peak at $2\theta=26.5°$) in the Mg/G composite completely disappears upon grinding of 1 h, and metallic magnesium (see peaks at 32.1, 34.3 and 36.6°) exist in a finely divided state. The diffraction peaks of magnesium broaden upon grinding; their analysis yields crystallite size estimates of 17–18 nm compared to 34 nm of magnesium as a starting material. However, $(Mg/G)_{none}$ prepared under these conditions had low specific surface area of 2.6 $m^2\,g^{-1}$ and a carbon monoxide uptake of only 7 μmol g^{-1} (Table 1). In contrast to $(Mg/G)_{CH}$ and $(Mg/G)_{THF}$ described below, no indication for a synergetic interaction between magnesium and graphite in $(Mg/G)_{none}$ seems to exist.

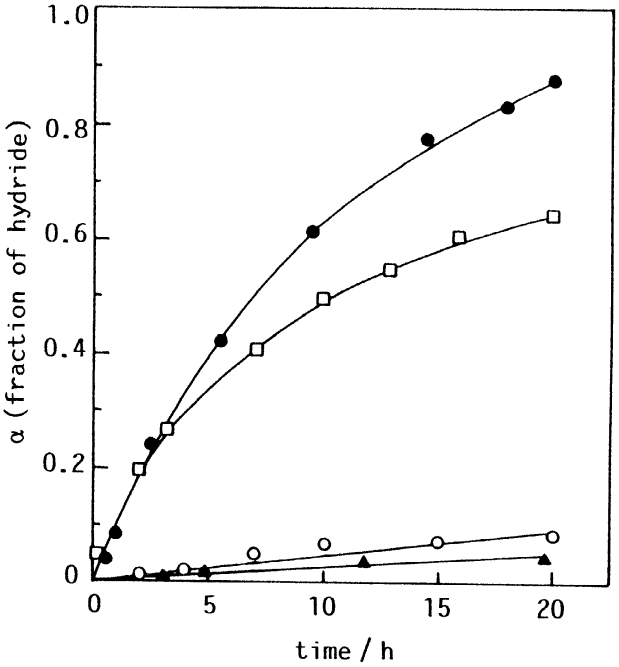

Fig. 1. Hydriding behavior of $(Mg/G)_{CH}$ and $(Mg/G)_{THF}$. ▲: $(Mg/G)_{none}$ (S-1); □: $(Mg/G)_{THF}$ (S-32); ○: $(Mg/G)_{CH}$ (S-41); ●: $(Mg/G)_{CH}$ (S-47). The samples were evacuated at 623 K for 2 h, followed by hydrogen at 66.7 kPa and 453 K.

The presence of CH or THF during grinding resulted in a drastic improvement of the hydriding properties of the composites. $(Mg/G)_{CH}$ and $(Mg/G)_{THF}$ revealed a high activity at much lower pressures and temperatures (66.7 kPa; 453 K) than reported previously. Magnesium powder as a starting material can be hydrided only with difficulty under 6 MPa at 674 K [10,13].

After MG, magnesium continues to exist in metallic form and XRD indicates no changes in lattice parameters of its hexagonal structure. In contrast to MG of magnesium and graphite without additives, the addition of CH or THF usually suppresses the crushing effect on magnesium and leads to a marked increase in the specific surface area of the resulting composite. This increase is mainly attributed to a degradation of the graphite structure as described later. The size reduction of the magnesium crystals generally stops as the amount of CH or THF added is increased (Table 1). This is unfavorable for the reaction of magnesium with hydrogen, but the activity of the composites for hydriding is greatly enhanced, especially in $(Mg/G)_{CH}$ (S-47) and $(Mg/G)_{THF}$ (S-32) as shown in Fig. 1. Active Mg/G composites can be formed efficiently only if ground in the presence of additives.

As shown by the XRD spectra, the layer structure of graphite in $(Mg/G)_{CH}$ and $(Mg/G)_{THF}$ was also destroyed by MG in the presence of CH or THF, while the specific surface area simultaneously increased to 40–90 $m^2\,g^{-1}$. From a comparison between S-1 and S-31 (S-3, -32, -42,

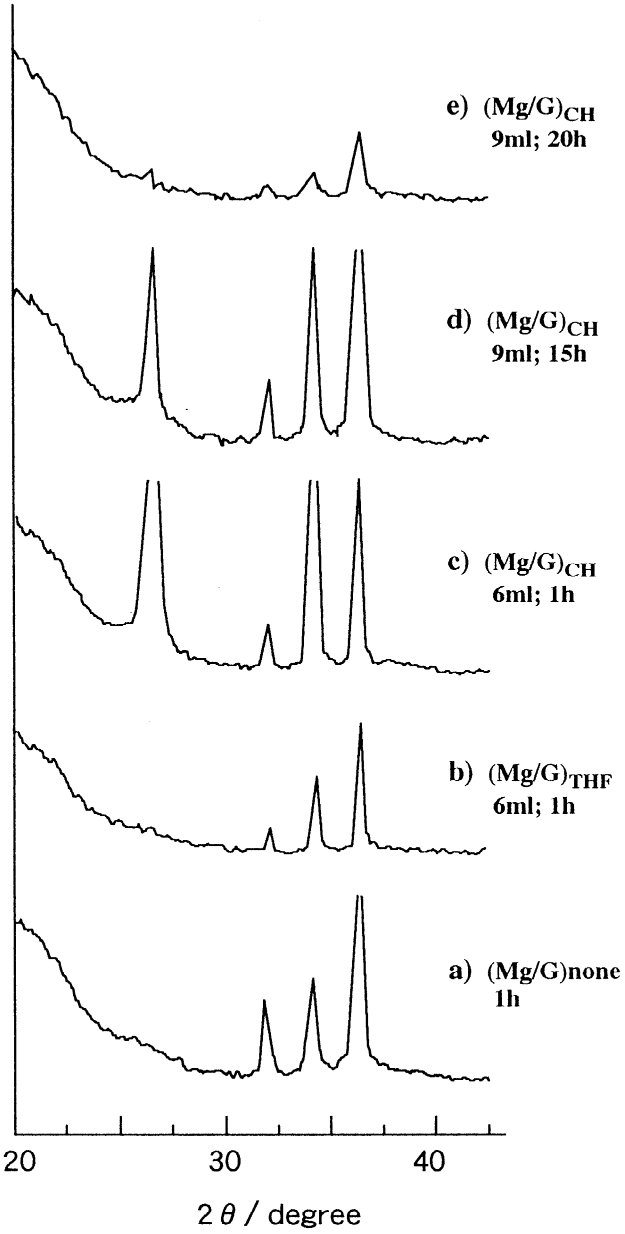

Fig. 2. XRD spectra of Mg/G composites: (a) $(Mg/G)_{none}$ (S-1), (b) $(Mg/G)_{THF}$ (S-32) and $(Mg/G)_{CH}$ (S-41, S-44 and S-46) after grinding of (c) 1 h, (d) 15 h and (e) 20 h, respectively. (CuK_{α} reactivation.)

-43, etc.), this increase is probably due to the degradation of the graphite rather than the magnesium structure during grinding. Furthermore, the layer structure of graphite degrades upon MG regardless of whether additives are present or not, but their presence appears to influence strongly the mode of degradation and this is likely to be the reason for the increase in surface area of the composites. However, $(Mg/G)_{CH}$ and $(Mg/G)_{THF}$ undergo quite different changes in their graphite structure upon grinding as shown by XRD (Fig. 2). For $(Mg/G)_{THF}$, the strong (002) diffraction peak of graphite at 26.5° completely disappeared with 1 h of MG accompanied by an increase in surface area, while the graphite structure in $(Mg/G)_{CH}$ still remained intact even after 17 h grinding. The chemical differences between CH and THF have been briefly discussed in a previous paper [8], but some questions still remain as to why easy degradation of graphite occurred in one case and not in the other.

Upon grinding in the presence of CH or THF, the carbon monoxide uptake which can be a guide to evaluate the surface activity of composites also increased. The hydriding behavior shown in Fig. 1 corresponds closely to the changes in CO chemisorption of the composites (Table 1) prepared under different conditions. THF exhibited more remarkable effects on CO chemisorption even in small amounts and in short periods of MG than CH. This might be related to structural differences as shown by the XRD patterns in Fig. 2. MG of magnesium and graphite in the presence of such additives resulted in an increase of surface area and CO uptake, leading to speculations about the mode of degradation of the graphite structure which might be different in the presence or the absence of additives. We suggested that graphite can play an important role in the formation of composites only if degraded by grinding in the presence of CH or THF [8,9]. This is closely associated with the differences in hydriding activity of the composites. The latter contain finely divided magnesium which is in intimate contact with decomposed graphite and synergetically constitutes active sites or phases for hydriding.

3.2. $(Mg/G)_{CH}$ and $(Mg/G)_{THF}$ composites

For $(Mg/G)_{CH}$ using CH of 9.0 cm^3, the size of the magnesium crystals decreased to 26 nm upon initial grinding (4 h), and reached a value of 15 nm after 20 h of grinding (Table 1). The surface area of the composite $(Mg/G)_{CH}$ gradually increased with increasing MG times, and reached nearly a maximum of about 60 $m^2 g^{-1}$. Compared to $(Mg/G)_{THF}$, the graphite structure in $(Mg/G)_{CH}$ (S-44) still remained to some extent and MG of more than 20 h was required for its complete degradation (Fig. 2); this is quite different from the results obtained by using THF. The hydriding activity of the composite $(Mg/G)_{CH}$ with 9 cm^3 of CH, also varied markedly with grinding and was highest after grinding for 17 h.

When the time period of MG was maintained at 20 h, the hydriding activity varied markedly as a function of CH volume (9–15 cm^3) added. It showed a maximum in $(Mg/G)_{CH}$ (S-47) with 12 cm^3 of CH and decreased upon further addition of CH. The surface area and CO uptake of $(Mg/G)_{CH}$ varied as a function of CH added, and was reflected by the hydriding behavior. From temperature-programmed desorption of hydrogen it was found that $(Mg/G)_{CH}$ (S-47) which showed a high activity for hydriding was also excellent for dehydriding.

As shown above, the optimum conditions for the formation of $(Mg/G)_{CH}$ and $(Mg/G)_{THF}$ were quite different (Table 1 Fig. 1). For $(Mg/G)_{THF}$, MG during 1 h with

Table 1
Characteristics of $(Mg/G)_{CH}$ and $(Mg/G)_{THF}^{a}$

Sample no.	Additive/cm^3	Grinding (min)	S_{BET} ($m^2 g^{-1}$)	Mg cryst. size (nm)	CO chemisorption ($\mu mol\ g^{-1}$)
S-1	none	60	2.6	17	7
S-31	THF/2.0	60	50	26	240
S-3	THF/4.5	60	40.5	26	266
S-32	THF/6.1	60	87	26	450
S-33	THF/9.0	60	–	–	3
S-41	CH/6.0	60	28	26	16
S-42	CH/9.0	240	51	26	44
S-43	CH/9.0	600	46	25	122
S-44	CH/9.0	900	54	20	276
S-45	CH/9.0	1020	44	19	312
S-46	CH/9.0	1200	63	15	10
S-47	CH/12	1200	60	15	258
S-48	CH/15	1200	52	19	101

[a] The composites were prepared by mechanical grinding of Mg (4.2 g) and graphite (1.8 g) in the presence of cyclohexane (CH) or tetrahydrofuran (THF).

6.1 cm^3 THF were optimal, while the formation of active $(Mg/G)_{CH}$ composites required prolonged grinding in the presence more than 6 cm^3 of CH; e.g., MG of 20 h and 12 cm^3 of CH. $(Mg/G)_{CH}$ (S-41) prepared by MG during 1 h and 6.0 cm^3 of CH was less active. For $(Mg/G)_{THF}$, prolonged grinding in the presence of larger amounts of THF lead to deactivation.

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