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Hydrogen-absorbing magnesium composites prepared by mechanical grinding with graphite: effects of additives on composite structures and hydriding properties

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Abstract

Novel Mg/G composites were prepared by mechanical grinding of magnesium (Mg) and graphite (G) with benzene as an additive. The addition of benzene was very important in determining the composite structures and hydriding properties. The composites prepared without benzene (designated hereafter as $(Mg/G)_{none}$) showed negligible activity for hydriding, whereas the use of benzene during grinding led to drastic changes in composite structures, leading to much improved hydriding. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy were used to characterize the structures of the Mg/G composites, especially for the mode of degradation of graphite structure during grinding. In the course of the composite formation in the presence of benzene (referred to as $(Mg/G)_{BN}$), the graphite structure was predominantly degraded by cleavages along graphite layers, while the graphite for $(Mg/G)_{none}$ was broken irregularly and disorderly, leading to rapid amorphization. Moreover, the additive for the composite formation plays an important role in promoting synergetic actions induced during the mechanical grinding of magnesium and graphite, in which the flaked graphite formed by fracture along graphite layers interacts with divided magnesium with charge-transfer. X-ray photoelectron spectroscopy (XPS) of $(Mg/G)_{BN}$ proved the charge-transfer from magnesium to graphite carbons. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Magnesium composites; Hydrogen absorption; Mechanical grinding; Ball mill; Graphite carbon

1. Introduction

In recent years, we have seen a considerable potential and intrinsic interest in the application of composites as hydrogen storage materials. It has been shown that the composites prepared by mechanical grinding of magnesium (Mg) and graphite (G) in the presence of organic additives (tetrahydrofuran, cyclohexane or benzene) are very effective as novel hydrogen storage materials [1–3]. The use of graphite is based on similarity to polycondensed ring compounds (e.g., anthracene, perylene and chrysene) which have proved to be effective for the chemical modification techniques developed for the improvement of hydriding properties of Mg-containing alloys [4–7]. The formation of Mg/G composites by the mechanical grinding using a planetary-type ball mill results in much improved hydriding–dehydriding properties of magnesium, although magnesium metal itself is hydrided with difficulty upon contact with hydrogen of 6 MPa at 673 K [8,9].

Previous investigations [1–3] revealed that the magnesium and graphite components are effectively converted into the Mg/G composites with enhanced hydriding characteristics only when ground in the presence of tetrahydrofuran, cyclohexane or benzene. In this paper, using XRD, TEM and Raman spectroscopy we investigate how mechanical grinding in the presence of such organic additives affects the structures and hydriding properties of the resulting Mg/G composites. Attention was specially directed toward the variations in the graphite structure during the mechanical grinding of magnesium and graphite in the presence of benzene as an additive. To further understand the effects of additives, we studied the characteristics of hydriding which reflected the composite structures of $(Mg/G)_{BN}$ and $(Mg/G)_{none}$ ground with and without benzene, respectively.

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2. Experimental

Magnesium (99.95%; 100 mesh) and graphite (grade, SP-1) were purchased from Rare Metallic and Union Carbide, respectively. Benzene was of research purity and further purified by distillation in the presence of sodium wire. The preparation of Mg/G composites was conducted by mechanical grinding using a planetary-type ball mill, the details of which have been previously described [1–3]. The preparation of all composite samples and their handling were carried out without exposure to air.

Hydrogen absorption measurements were made using volumetric equipment of glass provided with a high vacuum system (~2.7×10^{-2} Pa). Prior to the measurements the sample was subjected to evacuation treatment at 453 K for 2 h and the absorption of hydrogen was initiated upon contact with hydrogen of 66.7 kPa at 453 K.

Carbon monoxide chemisorption and surface areas were measured with ordinary techniques, the details of which have been described elsewhere [1]. Raman spectroscopy and XPS were studied with a Jasco Model NR-1800 spectrophotometer and a Fisons ESCALAB 210, using Mg Kα radiation, respectively. XRD spectra were recorded on a Rigaku diffractometer (RINT2200YS) using Cu Kα radiation.

3. Results and discussion

We have reported that the conditions (compositions, additives and grinding time) adopted when magnesium and graphite are mechanically ground are important in determining the characteristics of the resulting Mg/G composites [1–3]. In particular, the organic compounds as an additive regulate the solid-phase reaction between magnesium and graphite, resulting in strong influence on the composite structures (microstructure, surface and interface state) and composite properties (hydriding and dehydriding, catalysis and interactions of Mg with graphite). For the preparation of the Mg/G composites, benzene (BN) as an additive was mainly examined here.

3.1. Mg/G composites prepared in the presence of benzene

The characteristics of the Mg/G composites prepared under different conditions are summarized in Table 1. The general properties of $(\mathrm{Mg/G})_{\mathrm{BN}}$ prepared by grinding with benzene were similar to those of Mg/G composites prepared using tetrahydrofuran or cyclohexane [1–3]. As shown in Fig. 1a, the hydriding activity of $(\mathrm{Mg/G})_{\mathrm{none}}$ prepared without additives was very low. $(\mathrm{Mg/G})_{\mathrm{none}}$ showed yields of only α=ca 0.05 after 20 h when brought into contact with hydrogen of 66.7 kPa at 453 K, where α is the fraction of component magnesium reacted with hydrogen. The presence of benzene (BN) during the mechanical grinding of magnesium and graphite resulted in a drastic change in hydriding properties of the composites; the hydriding behavior was markedly improved. The hydriding activity varied with changes in amounts (0–12 cm^3) of benzene and passed through a maximum at 8 cm^3 of benzene when the period of grinding was maintained at 15 h (Fig. 1a). The activity of $(\mathrm{Mg/G})_{\mathrm{BN}}$ with benzene of 8 cm^3 increased markedly with grinding time to reach a maximum at 20 h of grinding (Fig. 1b).

Table 1
Characteristics of the composites $(\mathrm{Mg/G})_{\mathrm{BN}}$ prepared using benzene[a]

Benzene (cm^3)	Grinding (h)	S_{BET} ($\mathrm{m}^2\ \mathrm{g}^{-1}$)	Mg crystal size (nm)	CO chemisorption (μmol g^{-1})
0	1	2.6	17	7
0	15	1.4	16	32
8.0	1	20	14	1.6
8.0	10	87	13	132
8.0	15	150	13	185
8.0	20	162	14	392
8.0	25	123	14	415
8.0	30	127	14	461
6.0	15	83	21	
10.0	15	111	21	475
20.0	15	92	15	288

[a] The composites were prepared by mechanical grinding of Mg (4.2 g) and graphite (1.8 g) in the presence of benzene (BN).

For $(\mathrm{Mg/G})_{\mathrm{none}}$, grinding of only 1 h led to the complete disappearance of (002) and (004) diffraction peaks (corresponding to 2θ=26.5 and 54.6°, respectively) which characterized the graphite structure (Fig. 2). In XRD for $(\mathrm{Mg/G})_{\mathrm{BN}}$, it was found that such diffraction peaks gradually decreased with grinding over 25 h. In both the composite samples, the layer structure of graphite component was finally decomposed with grinding. Metallic magnesium (observed at 32.1, 34.3 and 36.6°) existed in a finely divided state upon mechanical grinding. According to powder X-ray diffraction, the magnesium crystallite sizes of $(\mathrm{Mg/G})_{\mathrm{BN}}$ were decreased to 13–21 nm compared to 34 nm of magnesium as a starting material (Table 1). In contrast to grinding without additives, the mechanical grinding in the presence of liquid additives is presumed to usually suppress crushing effects owing to reducing mechanical energy, but not necessarily in this case. The addition of benzene, as well as tetrahydrofuran [1,2] and cyclohexane [3], led to a marked increase in specific surface areas of $(\mathrm{Mg/G})_{\mathrm{BN}}$ to reach a 162 $\mathrm{m}^2\ \mathrm{g}^{-1}$ maximum value. This was in contrast to only 1.4–2.6 $\mathrm{m}^2\ \mathrm{g}^{-1}$ for $(\mathrm{Mg/G})_{\mathrm{none}}$ after grinding of 15 h. Possibly the increase in surface areas of $(\mathrm{Mg/G})_{\mathrm{BN}}$ is mainly attributed to differences in modes of the degradation of graphite structure as described in the next section.

It has been shown that solvated magnesium particles

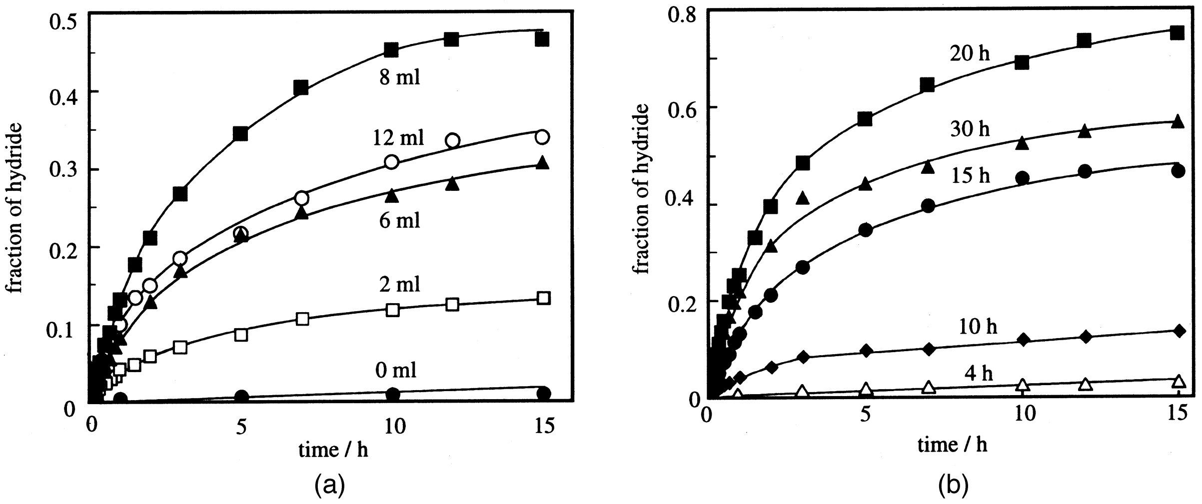

Fig. 1. Hydriding behavior of $(Mg/G)_{BN}$. (a) Effects of amounts of benzene (0–12 cm^3) used for the composite formation. (b) Effects of grinding time (4–30 h). The Mg/G composites were prepared by grinding of Mg (4.2 g) and graphite (1.8 g) with benzene. Hydrogen absorption: H_2=66.7 kPa; 453 K.

obtained when Mg metal vapor is dispersed into a low-temperature organic matrix (tetrahydrofuran, benzene or hexane) at 78 K are extremely active for hydriding [10–13]. For the magnesium component in $(Mg/G)_{BN}$, the organic additives are probably effective for enhancement of the dispersion of Mg metal particles during the mechanical grinding. This also leads to enhanced hydriding behavior as shown in Fig. 1.

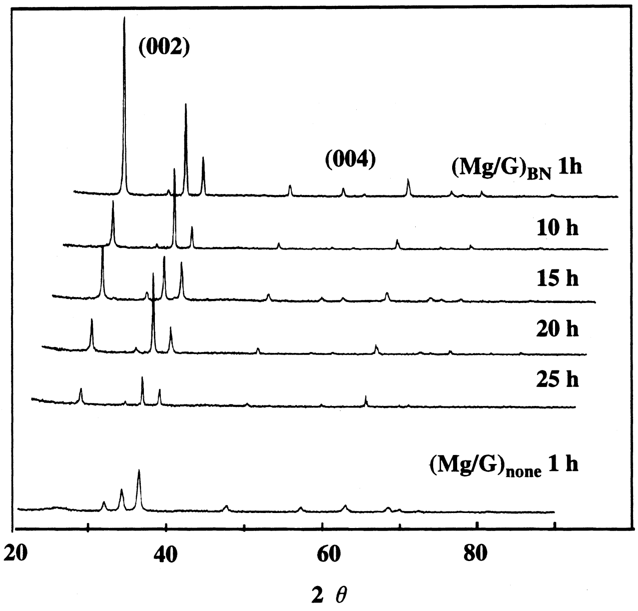

Fig. 2. XRD spectra of Mg/G composites. $(Mg/G)_{BN}$ was prepared by grinding of Mg (4.2 g) and graphite (1.8 g) with benzene (8 cm^3) for 1–25 h. $(Mg/G)_{none}$ was prepared by grinding of Mg (4.2 g) and graphite (1.8 g) without benzene for 1 h.

3.2. Effects of additives on graphite in Mg/G composites

Raman spectroscopy has been used to study the structural characterization of various carbon materials, such as graphite, glassy carbon or carbon fiber. Fig. 3 shows

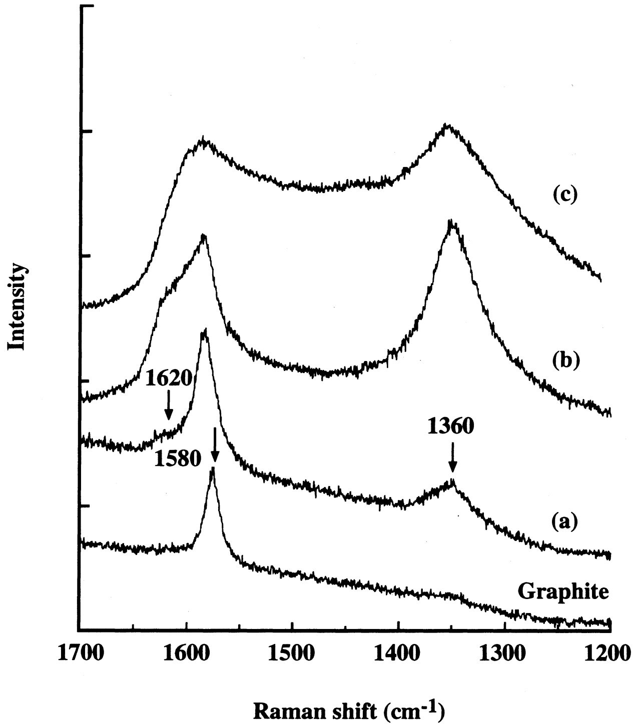

Fig. 3. Raman spectra of $(Mg/G)_{BN}$. $(Mg/G)_{BN}$ was prepared by grinding of Mg (4.2 g) and graphite (1.8 g) with benzene (8 cm^3) for (a) 10 min, (b) 1 h and (c) 25 h.

Raman spectra of the $(Mg/G)_{BN}$ composites prepared under different conditions, in comparison with those of original graphite. Graphite as a starting material exhibited a characteristic Raman band at 1580 cm^{-1}. Upon mechanical grinding, a new band appeared at 1360 cm^{-1}, which was assigned to a vibrational mode originating from the distorted hexagonal lattice of graphite near the crystal boundary [14,15]. Another Raman band also appeared at 1620 cm^{-1}, which seemed to be associated with structural defects introduced into graphite in the course of mechanical grinding. The intensity of these bands for $(Mg/G)_{BN}$ gradually increased with grinding and became stronger than that of the 1580 cm^{-1} graphite band after a prolonged grinding time. For $(Mg/G)_{none}$, a similar tendency was observed, but the degree of changes in the intensity of the Raman bands was more pronounced. The spectra of $(Mg/G)_{none}$ and $(Mg/G)_{BN}$ after mechanical grinding of 1 and 25 h, respectively, were very similar to those of amorphous carbons. This indicates that the defect structures increase in the graphite component to finally change to amorphous state as the mechanical grinding was continued. In XRD spectra of $(Mg/G)_{BN}$ ground with benzene of 8 cm^3 for a short time, negligible changes in diffraction peaks assigned to graphite structure were observed, but the Raman spectra showed that even upon grinding for only 10 min the structural defects already developed in graphite crystals (Fig. 3). Since Raman spectroscopy is normally sensitive to changes in surface layer (10–10^2 nm), this strongly suggests that the structural degradation of graphite occurs gradually from the vicinity of surfaces. For $(Mg/G)_{none}$, an increase in intensity of the 1360 cm^{-1} band was much more pronounced than that for $(Mg/G)_{BN}$; amorphization of graphite for $(Mg/G)_{none}$ more quickly progressed as expected from changes in XRD (Fig. 2).

It has been shown that the relative intensity ratios (I_{1360}/I_{1580}) of the 1360 cm^{-1} band to the 1580 cm^{-1} band can be used as an indication for perfection of the graphite layer structure, reflecting the proportions of edge plane or boundary of graphite crystal faces [16]. The half-band widths ($\Delta\nu_{1580}$) of the 1580 cm^{-1} band can be also a guide to evaluate the degree of graphitization. As shown in Fig. 4, the I_{1360}/I_{1580} ratios for $(Mg/G)_{none}$ rapidly increased to reach ca 1.1 upon initial grinding of 10 min, and afterward remained nearly unchanged, while for $(Mg/G)_{BN}$ the ratios gradually increased over 4 h and led to a steady value of about 0.95. Moreover, for $(Mg/G)_{none}$ and $(Mg/G)_{BN}$, the variations in $\Delta\nu_{1580}$ as a function of grinding time strongly suggested that the drop in the degree of graphitization was more pronounced for $(Mg/G)_{none}$ than for $(Mg/G)_{BN}$. These differences between $(Mg/G)_{none}$ and $(Mg/G)_{BN}$ probably reflect the mode of the structural degradation of graphite layers by the mechanical grinding. Thus, the degradation of graphite in the $(Mg/G)_{BN}$ composites predominantly occurs by cleavage along graphite layers, while the graphite for $(Mg/G)_{none}$ is broken irregularly and disorderly, leading to rapid amorphization. It now seems quite certain that the additives used for the mechanical grinding are very important in determining the structural characteristics of Mg/G composites. This is closely related to serious differences in surface areas between $(Mg/G)_{none}$ and $(Mg/G)_{BN}$.

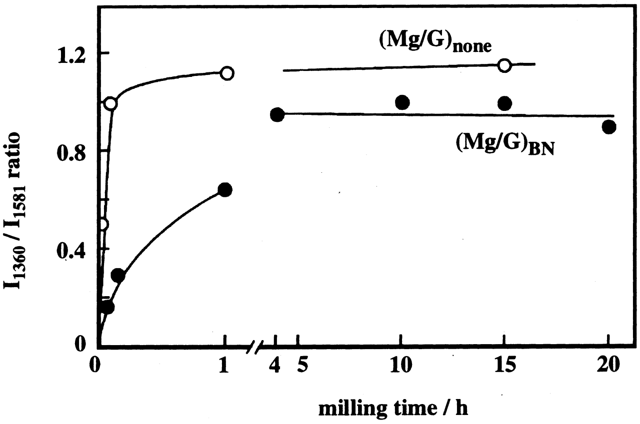

Fig. 4. I_{1360}/I_{1580} ratios versus grinding time for $(Mg/G)_{none}$ and $(Mg/G)_{BN}$. $(Mg/G)_{none}$ and $(Mg/G)_{BN}$ were prepared by grinding with benzene of 0 and 8 cm^3, respectively.

A remarkable feature of the Mg/G composites is that the active composites as a hydrogen absorber are formed more efficiently only when ground with benzene, tetrahydrofuran or cyclohexane [1–3]. Thus, graphite broken along cleavage planes is effectively operative for hydriding of the Mg/G composites. The catalytic properties of the composites, such as catalytic activation of hydrogen and CO chemisorption, were also enhanced upon grinding with such organic additives; magnesium or graphite alone did not show any catalytic activity, nor did the Mg/G composites prepared without such additives (H. Imamura, unpublished data). These facts strongly indicate that the additives for the Mg/G composites play an important role in promoting synergetic actions induced during grinding of magnesium and graphite, in which flaking of graphite by fracture along graphite layers preferentially occurs to interact with finely divided magnesium with charge-transfer. As shown in Table 2, XPS studies of $(Mg/G)_{BN}$, as well as $(Mg/G)_{CH}$ prepared using cyclohexane (CH) [3], support the existence of charge-transfer from magnesium to graphite carbons to some extent, as opposed to $(Mg/G)_{none}$.

TEM observations of $(Mg/G)_{BN}$ and $(Mg/G)_{none}$ are consistent with the above conclusion. TEM of $(Mg/G)_{BN}$ ground with benzene for 25 h is shown in Fig. 5. The graphite component proved to be dispersed on magnesium particles in a state of cleaved lamella with nanocrystal size. Magnified TEM of the lamella shows that the cleaved graphite layers were estimated to be about 20 nm thickness

Table 2
XPS results of various Mg/G composites

Sample	Binding energy (eV Mg 2p)
Mg	49.80
$(Mg/G)_{none}$ [a]	49.60
$(Mg/G)_{BN}$ [b]	50.12
$(Mg/G)_{CH}$ [c]	50.40

[a] By grinding of Mg (4.2 g) and graphite (1.8 g) without additives.

[b] By grinding of Mg (4.2 g) and graphite (1.8 g) with benzene (8 cm^3) for 15 h.

[c] By grinding of Mg (4.2 g) and graphite (1.8 g) with cyclohexane (12 cm^3) for 20 h.

on the *z*-axis. From TEM for $(Mg/G)_{none}$, such lamellar structures of graphite were not observed at all. Thus, the graphite structure of $(Mg/G)_{none}$ was completely degraded to amorphous by the mechanical grinding compared to that for $(Mg/G)_{BN}$, in which the organic additives assist to transform the graphite into thin flakes.

Fig. 5. TEM of $(Mg/G)_{BN}$ with magnifications of 2×10^5. $(Mg/G)_{BN}$ was prepared by grinding of Mg (4.2 g) and graphite (1.8 g) with benzene (8 cm^3) for 25 h.

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