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Journal of Alloys and Compounds 330–332 (2002) 579–583

Journal of ALLOYS AND COMPOUNDS

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# Composites for hydrogen storage by mechanical grinding of graphite carbon and magnesium

Hayao Imamura*, Shinya Tabata, Noriko Shigetomi, Yoshirou Takesue, Yoshihisa Sakata

*Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan*

## Abstract

Novel hydrogen storage Mg/G nano-composites obtained by mechanical grinding of magnesium (Mg) and graphite carbon (G) with organic additives (benzene, cyclohexane or tetrahydrofuran) have been characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC) and temperature programmed desorption (TPD) techniques. The occurrence of various effects as a result of the formation of Mg/G composites ground with benzene, cyclohexane or tetrahydrofuran (designated hereafter as $(Mg/G)_{BN}$, $(Mg/G)_{CH}$ or $(Mg/G)_{THF}$, respectively) is expected. Upon mechanical grinding with benzene or cyclohexane for 4–40 h, new hydrogen-storing sites, other than those due to the magnesium component, were formed in the Mg/G composites and they took up hydrogen reversibly. The cleavage-degraded graphite in the composites plays an important role in such hydrogen uptake and release. The formation of Mg/G composites upon grinding with the organic additives led to not only a drop in the onset temperature of $MgH_2$ decomposition, but the formation of additional hydrogen uptake sites. In marked contrast to $(Mg/G)_{BN}$ and $(Mg/G)_{CH}$, the composites ground without any additives (referred as $(Mg/G)_{none}$) did not show such behavior. The effective nano-composites are those in which there are synergetic interactions between magnesium and graphite as a result of mechanical grinding with the organic additives.

*Keywords:* Composites; Magnesium; Graphite carbon; Hydrogen storage; Ball-milling

## 1. Introduction

Much efforts have been concentrated on studies of metal hydrides as hydrogen storage, in which magnesium metal and magnesium-containing alloys are considered as promising candidate materials [1]. Recently, new carbon materials, e.g., carbon nanotubes [2,3] and graphite nanofibers [4,5], have become of interest for possible use in hydrogen storage.

We have proposed the application of nano-composites, obtained by mechanical grinding of magnesium (Mg) and graphite carbon (G) with organic additives (tetrahydrofuran, cyclohexane or benzene) using a planetary-type ball mill, as novel hydrogen storage materials [6–11]. In the mechanical grinding of magnesium and graphite, the use of the organic additives is very important in determining the characteristics of the resulting Mg/G composites. The organic additives control the solid-phase reaction between magnesium and graphite during grinding, leading to strong influence on the microstructures of composites, especially graphite structure, and the hydriding–dehydriding properties [8]. The occurrence of various effects as a result of the formation of nano-composites is expected; the graphite carbon in $(Mg/G)_{BN}$ and $(Mg/G)_{CH}$ is proved to be additionally endowed with the capability for hydrogen storage. In this paper, we report experimental findings that new hydrogen-storing sites, other than those due to the magnesium component, are formed during grinding of Mg and graphite with benzene or cyclohexane and that these sites reversibly take up hydrogen.

## 2. Experimental procedures

Magnesium (99.95%; 100 mesh) and graphite (grade: SP-1) were used as obtained from Rare Metallic and Union Carbide, respectively. Benzene (BN), cyclohexane (CH) and tetrahydrofuran (THF) were purified by distillation in the presence of sodium wire. The preparation of Mg/G composites was carried out by mechanical grinding using a planetary-type ball mill (High G: BX 254; Kurimoto), being capable of operating at 863 rpm. Magnesium powder

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*Corresponding author. Tel.: +81-836-85-9680; fax: +81-836-85-9601.

*E-mail address:* hi-khm@po.cc.yamaguchi-u.ac.jp (H. Imamura).

0925-8388/02/$ – see front matter
PII: S0925-8388(01)01506-7

(4.2 g) and graphite (1.8 g) were placed in a stainless steel container (160 cm$^3$; lined with zirconia) with zirconia balls (3 mm in diameter; 224 g) under a dry nitrogen atmosphere. The mixtures were subjected to mechanical grinding with and without benzene, cyclohexane or tetrahydrofuran to yield the Mg/G composites, referred to hereafter as $(Mg/G)_{BN}$, $(Mg/G)_{CH}$, $(Mg/G)_{THF}$ or $(Mg/G)_{none}$, respectively.

DSC measurements were made on a TA Instruments 910S with Thermal Analyst 2200 system.

## 3. Results and discussion

X-ray diffraction (XRD) patterns revealed structural decomposition of the graphite component in the composites during grinding [6–11]. However, there was a great difference in the modes of the degradation of graphite structure between the Mg/G composites ground with and without the organic additives. Raman spectroscopic measurements have proved that upon mechanical grinding, the structural degradation of graphite in the $(Mg/G)_{BN}$ composite predominantly occurs by cleavage along graphite layers, while the graphite in $(Mg/G)_{none}$ is broken irregularly with no discernible order, leading to rapid amorphization [8]. TEM photographs of both the composites were consistent with the above discussion. These structural differences in decomposed graphite reflected the surface area and pore size distribution obtained by nitrogen adsorption isotherms; the surface areas for $(Mg/G)_{none}$ ground without any additives were only 1.4–2.6 m$^2$ g$^{-1}$ with pore radii distributed around 1.8 nm, while those for $(Mg/G)_{BN}$ and $(Mg/G)_{CH}$ were 51–162 m$^2$ g$^{-1}$ with smaller radii around 0.8 nm.

In electronic properties, only cleavage-degraded graphite in $(Mg/G)_{BN}$ intimately interacted with finely divided magnesium with charge-transfer as evidenced by XPS, in contrast to the graphite in $(Mg/G)_{none}$. In XPS for $(Mg/G)_{BN}$ and $(Mg/G)_{CH}$, the binding energy of Mg 2p was shifted 0.5–0.8 eV to higher energies [8], compared with that for $(Mg/G)_{none}$; incidentally, the Mg 2p for $(Mg/G)_{none}$ was not shifted and was almost identical to that for Mg itself. It has been shown that such charge-transfer sites formed between aromatic carbons and alkali metals exhibit the catalytic ability to activate hydrogen molecules and to hydrogenate olefin without difficulty [12]. Actually $(Mg/G)_{BN}$ $(Mg/G)_{CH}$ and $(Mg/G)_{THF}$ readily catalyzed the hydrogenation of ethene at room temperature, whereas $(Mg/G)_{none}$ was completely inactive (Table 1). This is consistent with catalysis by electron donor–acceptor complexes with charge-transfer.

These facts reflect differences in reaction behavior with hydrogen between the Mg/G composites ground with and without organic additives. It now seems quite certain that upon grinding with tetrahydrofuran, benzene or cyclohexane a synergism between graphite and magnesium develops, leading to the enhanced hydrogen-storing properties for the resulting Mg/G composites [6–11]. The hydriding activity of the magnesium component in the composites is much better than reported previously [13].

Table 1
Hydrogenation of ethene on $(Mg/G)_{THF}$, $(Mg/G)_{BN}$, $(Mg/G)_{CH}$ and $(Mg/G)_{none}$ [a]

| Sample | Activity (mmol min$^{-1}$ g$^{-1}$) |
|---|---|
| $(Mg/G)_{none}$ | No reaction |
| $(Mg/G)_{THF}$ | $4.8\times10^{-3}$ |
| $(Mg/G)_{BN}$ | $4.9\times10^{-3}$ |
| $(Mg/G)_{CH}$ | $1.2\times10^{-3}$ |

[a] The reaction was carried out at 298 K with ethene (20 Torr) and hydrogen (40 Torr).

For $(Mg/G)_{BN}$ and $(Mg/G)_{none}$ samples previously exposed to hydrogen of 3 MPa, differential scanning calorimeter (DSC), which was measured at a scanning rate of 5.0 K min$^{-1}$ under a 0.1 MPa hydrogen atmosphere, showed characteristic endothermic peaks (Fig. 1). When pure magnesium powder was used for comparison, DSC indicated that the peak temperature of $MgH_2$ decomposition was 707 K, close to the results reported by Huot et al.

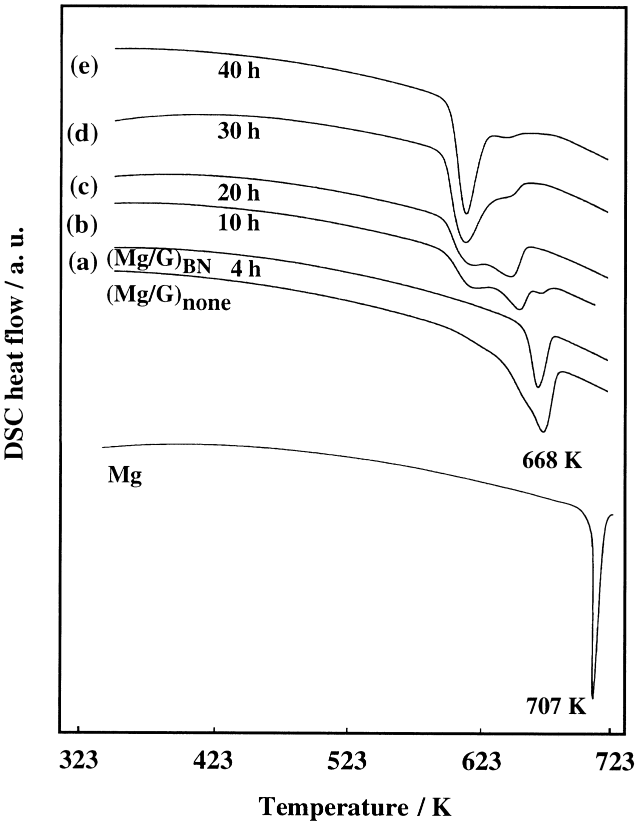

Fig. 1. DSC traces for various $(Mg/G)_{BN}$, $(Mg/G)_{none}$ and Mg samples. The $(Mg/G)_{BN}$ composites were prepared by grinding with benzene (8.0 cm$^3$) for (a) 4 h, (b) 10 h, (c) 20 h, (d) 30 h and (e) 40 h. $(Mg/G)_{none}$ was prepared by grinding without benzene for 15 h.

[14]. The DSC trace of $(Mg/G)_{none}$ exhibited a broad endothermic peak at 668 K which was similarly assigned to the decomposition of $MgH_2$ from XRD. It seems that magnesium particles with cracked irregular surface produced by the ball milling technique show improved hydriding–dehydriding kinetics [15].

The mechanical grinding with benzene led to significant changes in DSC behavior. A very important characteristic of the DSC traces for $(Mg/G)_{BN}$, prepared by varying grinding times (4–40 h), is that they indicate a series of transformations leading to the formation of composites during grinding. Mechanical grinding of $(Mg/G)_{BN}$ for 4 h led to a DSC peak at about 664 K (Fig. 1a). As only magnesium hydride was identified in the XRD pattern of the sample, this endothermic peak was assigned to decomposition of the hydride. Upon grinding for 10 h or longer, new endothermic peaks, other than that due to the decomposition of $MgH_2$ appeared. The DSC traces, notably the numbers and temperatures of peaks, changed significantly with grinding. Grinding for 40 h caused all but single peak again (Fig. 1e). This was also found to be due to decomposition of $MgH_2$ by reference to the XRD pattern of the sample. For $(Mg/G)_{BN}$, the endothermic DSC peaks corresponding to decomposition of the magnesium hydride were obviously shifted to lower temperatures as the grinding times were prolonged. To clarify what causes the changes in the DSC traces, temperature programmed desorption (TPD) measurements for the same $(Mg/G)_{BN}$ samples were made in vacuo at a heating rate of 2.5 K $min^{-1}$ by continuously monitoring desorbed hydrogen via quadrupolar mass spectrometer. As shown in Fig. 2, the TPD results gave a good correspondence with the DSC results (Fig. 1) for each sample; both displayed similar peak shapes and approximately the same number of peaks. This proves that newly emerged DSC peaks of $(Mg/G)_{BN}$ (b, c and d in Fig. 1) are derived from endothermically desorbed hydrogen. It is further confirmed by the fact that $(Mg/G)_{BN}$ obtained by grinding for 10 h showed essentially reproducible DSC traces in repeated scans when hydrogenated under 3 MPa of hydrogen, followed by continuous heating from 350 to 700 K under a hydrogen pressure of 0.1 MPa (Fig. 3).

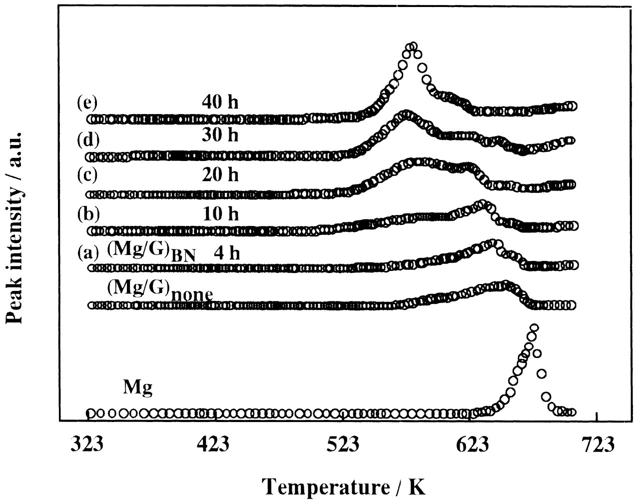

Fig. 2. TPD of various $(Mg/G)_{BN}$, $(Mg/G)_{none}$ and Mg samples. The $(Mg/G)_{BN}$ composites were prepared by grinding with benzene (8.0 $cm^3$) for (a) 4 h, (b) 10 h, (c) 20 h, (d) 30 h and (e) 40 h. $(Mg/G)_{none}$ was prepared by grinding without benzene for 15 h.

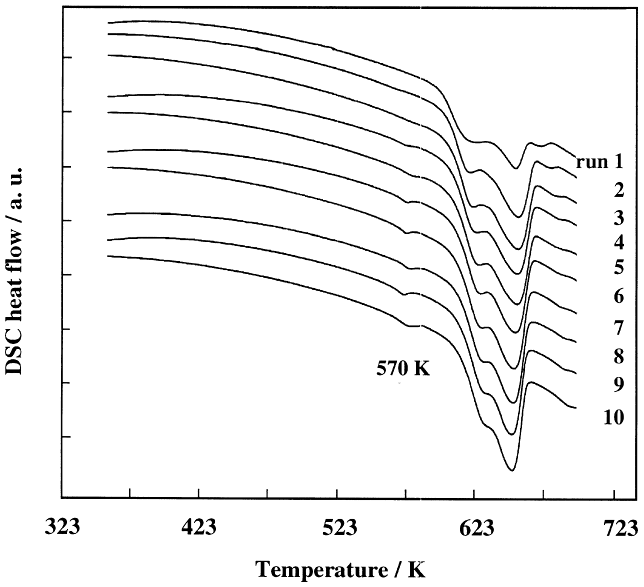

Fig. 3. Repeated DSC measurements (runs 1–10) on $(Mg/G)_{BN}$, prepared by grinding with benzene (8.0 $cm^3$) for 10 h.

The DSC traces were significantly dependent upon hydrogen pressure applied to the sample beforehand. For $(Mg/G)_{BN}$ ground for 20 h, applying hydrogen pressure up to 0.5 MPa gave a single DSC peak only, which was assigned to the decomposition of $MgH_2$. As shown in Fig. 4, upon applying hydrogen pressure of more than 0.7 MPa,

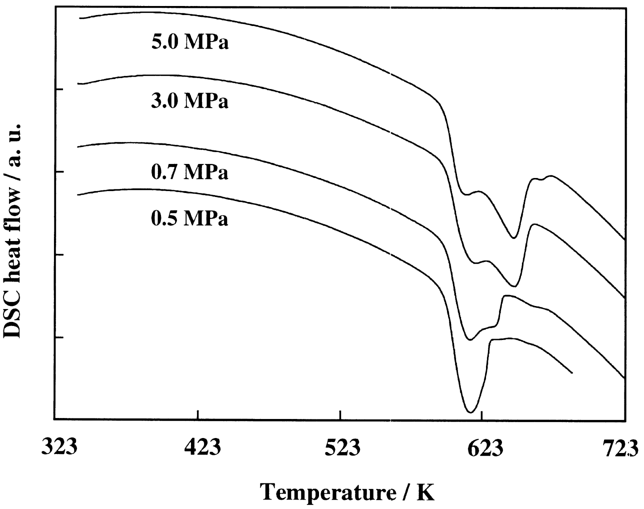

Fig. 4. Influences of hydrogen pressure applied on the DSC traces of $(Mg/G)_{BN}$, prepared by grinding with benzene (8.0 $cm^3$) for 20 h. DSC was measured under 0.1 MPa of hydrogen.

new endothermic peaks began to appear and increased with hydrogen pressure applied. TPD of $(Mg/G)_{BN}$ to which hydrogen pressures of 0.067, 1, 3 or 5 MPa were applied were also consistent with the DSC traces.

These results give evidence that there are several types of magnesium with different properties or that hydrogen storage by sites other than the magnesium component simultaneously occurs, in which the pressure dependence of hydrogen uptake was observed. In a previous paper [8], the quantitative measurements of $H_2$ uptake by $(Mg/G)_{BN}$ have been carried out at hydrogen pressure of 0.067 MPa. By considering the results obtained here, all the hydrogen taken up under a 0.067 MPa hydrogen atmosphere is considered to react with the magnesium component to form the hydride; the amounts of hydrogen absorption by magnesium at 453 K reached as much as about 1.5 in H/Mg after 15 h, as shown in Fig. 1 of Ref. [8].

Another interesting feature of the hydrogen uptake by $(Mg/G)_{BN}$, $(Mg/G)_{THF}$ and $(Mg/G)_{CH}$ is that for the repeated cycles (e.g. as shown in Fig. 3 for $(Mg/G)_{BN}$), an additional endothermic peak was observed (around 570 K for $(Mg/G)_{BN}$) and it gradually became large with cycles. The appearance of this peak was closely associated with thermal treatment of $(Mg/G)_{BN}$, $(Mg/G)_{THF}$ and $(Mg/G)_{CH}$; thus the peak intensity increased with increasing pretreatment temperature of 673–773 K. When DSC for $(Mg/G)_{CH}$ was measured under 3 or 6 MPa of hydrogen (Fig. 5), the peaks for the decomposition and formation of $MgH_2$ were observed around 727 and 691 K, respectively. Moreover, a set of DSC peaks around 673 and 596 K is characterized as reversible hydrogen release and uptake, respectively. The temperatures for hydrogen uptake and release were obviously lower than thermodynamic absorption and desorption temperatures of Mg–H system at 3 MPa of hydrogen. Thus this suggests the existence of hydrogen other than that due to the formation and decomposition of $MgH_2$; the cleavage-degraded graphite in the composites plays an important role in the hydrogen uptake and release observed here. When the DSC traces were measured under a hydrogen atmosphere of 6 MPa, the hydrogen uptake and release were shifted to higher temperatures. The $H_2$ uptake and release were clearly ascertained at 563 and 695 K in the process of rising temperature, respectively, and during a subsequent lowering of temperature the $H_2$ uptake at 642 K was observed again. The $H_2$ uptake discovered here is characterized by excellent reversibility and marked pressure dependence.

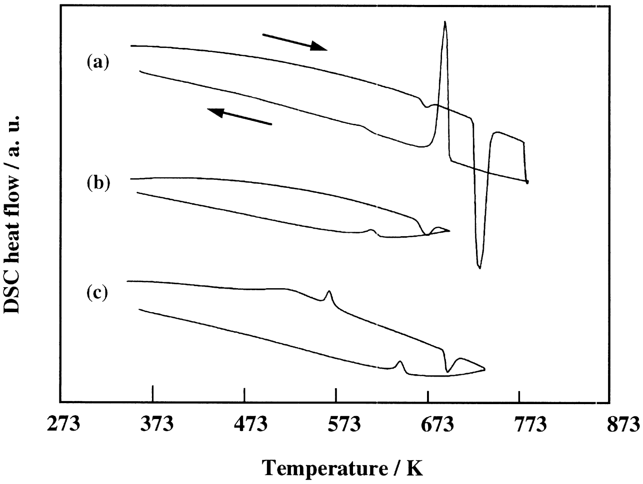

Fig. 5. DSC traces for $(Mg/G)_{CH}$, prepared by grinding with cyclohexane (15 $cm^3$) for 40 h. DSC was scanned (a) between 343 and 773 K under 3 MPa of $H_2$, (b) between 343 and 693 K under 3 MPa of $H_2$ and (c) between 343 and 733 K under 6 MPa of $H_2$.

Unlike $(Mg/G)_{BN}$, $(Mg/G)_{THF}$ and $(Mg/G)_{CH}$, $(Mg/G)_{none}$ did not show such hydrogen uptake and release other than those due to the formation and decomposition of $MgH_2$, respectively. Pure graphite itself and graphite subjected to grinding with benzene did not take up hydrogen; neither showed only DSC response. The effective $(Mg/G)_{BN}$, $(Mg/G)_{CH}$ and $(Mg/G)_{THF}$ composites are those in which there are synergetic interactions between magnesium and graphite carbon as a result of mechanical grinding with the organic additives. The formation of Mg/G composites upon such grinding led to not only a drop in the onset temperature of $MgH_2$ decomposition, but the formation of additional hydrogen-storing sites in the Mg/G composites. Perhaps the cleavage-degraded graphite is deeply involved in such hydrogen uptake, other than that due to magnesium.

## Acknowledgements

This work has been supported in part by a Grant-in-Aid for Scientific Research on Priority Area (No. 299) from the Ministry of Education, Science, Sports and Culture, Government of Japan.

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