Hydrogen storage composites obtained by mechanical grinding of magnesium with graphite carbon

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Novel hydrogen storage Mg/G composites prepared by mechanical grinding of magnesium (Mg) and graphite carbon (G) with benzene have been found to incorporate new hydrogen-storing sites, other than those due to the magnesium component, and can take up hydrogen reversibly.

Much research effort has been concentrated on the storage of hydrogen in metals, for which magnesium metal and magnesium-containing alloys are considered promising candidate materials.[1] Recently, new carbon materials, *e.g.* carbon nanotubes [2] and graphite nanofibers,[3] have become of interest for possible use in hydrogen storage.

We have proposed the application of composites, prepared by mechanical grinding of magnesium (Mg) and graphite carbon (G) in the presence of organic additives (tetrahydrofuran, cyclohexane or benzene) using a planetary-type ball mill, as novel hydrogen storage materials.[4–7] In the mechanical grinding of magnesium and graphite for Mg/G composite formation, the presence of the organic additives is important in determining the characteristics of the resulting composites. Such organic compounds regulate the solid-phase reaction between magnesium and graphite carbon during grinding, leading to a strong influence on the composite structures and the hydriding–dehydriding properties of the magnesium component. The hydriding activity of these composites is much better than reported previously.[8] In this communication, we report experimental findings that new hydrogen-storing sites, other than those due to the magnesium component in the composites, are formed during grinding in the presence of benzene and that these sites reversibly take up hydrogen.

X-Ray diffraction (XRD) patterns revealed decomposition of the graphite component in the composites with grinding.[4–7] However, there was a great difference in the modes of degradation of the graphite structure between the Mg/G composites ground with and without the organic additives. Raman spectroscopy has proved that upon mechanical grinding, the structural degradation of graphite in the $(Mg/G)_{BN}$† composite predominantly occurs by cleavage along the graphite layers, while the graphite in $(Mg/G)_{none}$† is broken irregularly with no discernible order, leading to rapid amorphization.[7] In marked contrast to the graphite in $(Mg/G)_{none}$, only the cleavage-degraded graphite intimately interacted with finely divided magnesium with charge-transfer as evidenced by XPS, developing a synergism which leads to the enhanced hydrogen-storing properties.[7] These facts reflect differences in hydrogenation behaviour between $(Mg/G)_{BN}$ and $(Mg/G)_{none}$.

For various $(Mg/G)_{BN}$ samples previously exposed to hydrogen at 3 MPa, differential scanning calorimetry (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.*[9] The DSC trace of $(Mg/G)_{none}$, ground without any additives, exhibited a broad endothermic peak at 668 K which was similarly assigned to the decomposition of MgH_2. It seems

that magnesium particles with cracked irregular surfaces produced by the ball milling technique show improved hydriding–dehydriding kinetics.[10]

The mechanical grinding with benzene led to significant changes in DSC behaviour. A very important characteristic of the DSC traces for $(Mg/G)_{BN}$, prepared at 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. 1(a)]. 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 resulted in the loss of all but one peak [Fig. 1(e)]. 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 DSC traces, temperature programmed desorption (TPD) measurements for the same $(Mg/G)_{BN}$ samples were made *in vacuo* by continuously monitoring desorbed hydrogen *via* quadrupolar
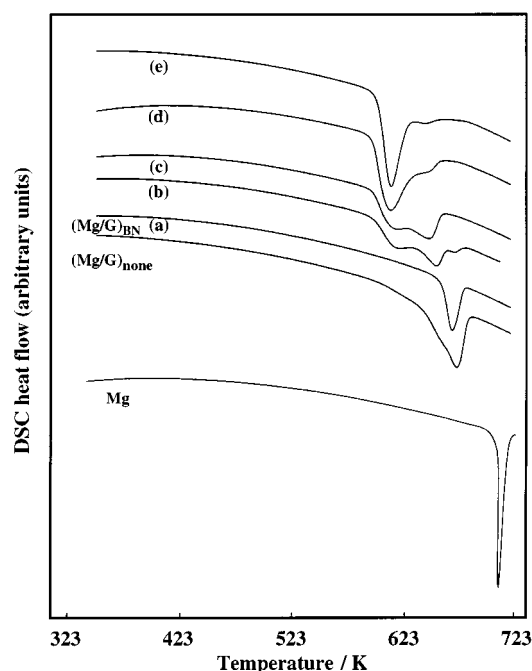

Fig. 1 DSC traces for various $(Mg/G)_{BN}$, $(Mg/G)_{none}$ and Mg samples. The $(Mg/G)_{BN}$ composites were prepared by grinding with benzene (8.0 cm³) for (a) 4 h, (b) 10 h, (c) 20 h, (d) 30 h and (e) 40 h. $(Mg/G)_{none}$ was prepared by grinding without benzene for 15 h.
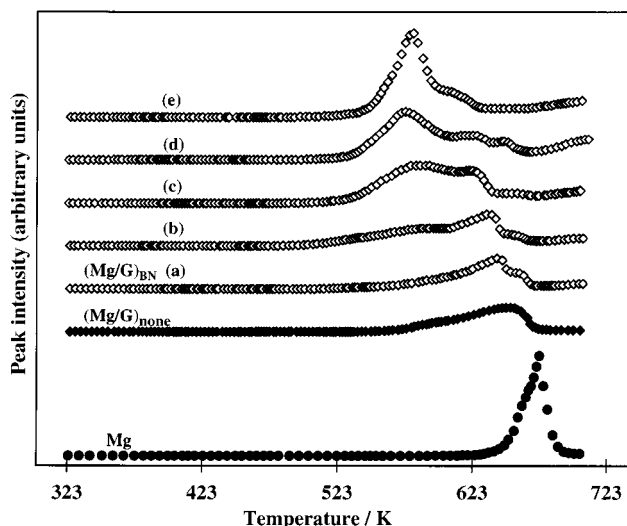
Fig. 2 TPD of various (Mg/G)$_{BN}$, (Mg/G)$_{none}$ and Mg samples. The (Mg/G)$_{BN}$ composites were prepared by grinding with benzene (8.0 cm^3) for (a) 4 h, (b) 10 h, (c) 20 h, (d) 30 h and (e) 40 h. (Mg/G)$_{none}$ was prepared by grinding without benzene for 15 h.

mass spectrometry. As shown in Fig. 2, the TPD results gave a good correspondence with the DSC measurements for each sample; both displayed similar peak shapes and approximately the same number of peaks. This proves that the newly emerged DSC peaks were derived from endothermically desorbed hydrogen. Further confirmation is provided by the fact that the DSC peaks of (Mg/G)$_{BN}$ prepared by grinding for 20 h are essentially reproducible in repeated scans of the same sample when pressurized under 3 MPa of hydrogen, followed by continuous heating from 350 to 700 K under a hydrogen pressure of 0.1 MPa, (Fig. 3).
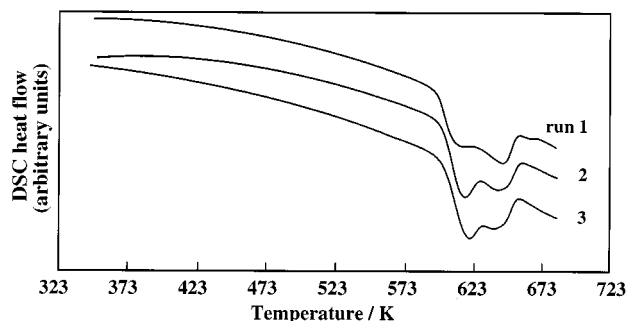

Fig. 3 Repeated DSC measurements (run 1–3) on (Mg/G)$_{BN}$, prepared by grinding with benzene (8.0 cm^3) for 20 h.

Another interesting feature of the hydrogen uptake by (Mg/G)$_{BN}$ is that the DSC traces were significantly dependent upon the pressure of hydrogen to which the sample had been exposed. For (Mg/G)$_{BN}$ ground for 20 h, exposure to hydrogen at pressures up to 0.5 MPa gave a single DSC peak only (Fig. 4), which was assigned to the decomposition of MgH$_2$. Upon exposure to hydrogen pressure of more than 0.7 MPa, new endothermic peaks other than that due to the decomposition of MgH$_2$ began to appear and increased with hydrogen pressure applied. These results give evidence that hydrogen storage by sites or phases other than those from the magnesium component simultaneously occurred, in which the pressure dependence of hydrogen uptake was observed. The proportion of additionally stored hydrogen can be roughly estimated from the DSC or TPD peak area; an approximate measurement corresponded to about 50% of the total hydrogen stored by (Mg/G)$_{BN}$ exposed to hydrogen at 3 MPa. The H$_2$ uptake discovered here is characterized by excellent reversibility and marked pressure dependence. However, there were no changes in the XRD patterns for variations in hydrogen pressure applied; only magnesium hydride was identified in the (Mg/G)$_{BN}$ composite.
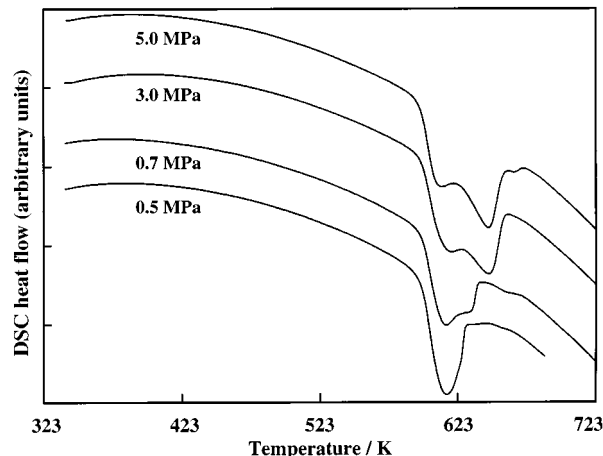

Fig. 4 Influence of hydrogen pressure applied to the sample on the DSC traces of (Mg/G)$_{BN}$, prepared by grinding with benzene (8.0 cm^3) for 20 h.

Exactly which sites in the composites store the additional hydrogen, or the method by which this occurs, is as yet unknown.

Pure graphite itself and graphite subjected to grinding did not take up hydrogen; neither showed any DSC response. (Mg/G)$_{none}$ did not show similar behaviour to that observed for (Mg/G)$_{BN}$. The most effective (Mg/G)$_{BN}$ composites are those in which there are synergic interactions between magnesium and graphite carbon as a result of mechanical grinding with benzene. 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 (Mg/G)$_{BN}$. However, as shown in Fig. 1(e) and 2(e), prolonged grinding led to detrimental effects on additional hydrogen uptake; the hydrogen-storing sites formed were decomposed. This is probably related to the extent of amorphization of the graphite component by excessive grinding.[7]

Notes and references

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