HYDROGEN STORAGE OF NANOSTRUCTURED CARBON COMPOSITES OBTAINED BY MECHANICAL GRINDING OF GRAPHITE AND MAGNESIUM

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Introduction

We have proposed the application of nanostructured carbon composites, obtained by mechanical grinding of graphite (G) and magnesium (Mg) with organic additives (tetrahydrofuran, cyclohexane or benzene) using a planetary-type ball mill, as novel hydrogen storage materials [1,2]. The role of the organic additives during ball milling is very important in determining the characteristics of the resulting Mg/G nanocomposites. The organic additives control the solid-phase reaction between graphite and Mg, leading to strong influence on the composite nanostructures and the H_2 uptake properties. The occurrence of various effects as a result of the formation of nanocomposites is expected; the graphite component in the composite is proved to be 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 Mg component, are formed during ball milling of graphite and Mg with benzene or cyclohexane and that these sites reversibly take up hydrogen.

Experimental

The Mg/G nanocomposites were prepared with a planetary-type ball mill (High G: BX 254; Kurimoto Ltd.), being capable of operating at 863 rpm. Graphite and Mg powders 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 ball milling with benzene or cyclohexane as an additive to yield the Mg/G nanocomposites, referred to hereafter as $(Mg/G)_{BN}$ or $(Mg/G)_{CH}$, respectively.

Differential scanning calorimeter (DSC) measurements were made on a TA Instruments 910S with Thermal Analyst 2200 system.

Results and Discussion

Ball milling of $(Mg/G)_{BN}$ for 4-40 h led to significant changes in DSC behavior, indicating a series of transformations leading to the formation of nanocomposites. Ball milling 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 ball milling 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 milling. Ball milling for 40 h caused all but single peak again (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 MgH_2 were obviously shifted to lower temperatures as the milling times were prolonged.

The formation of Mg/G nanocomposites upon ball milling with the organic additives led to not only a drop in the decomposition temperature of MgH_2, but also additional hydrogen uptake by the composites [2].

An interesting feature of $(Mg/G)_{BN}$ is that for the repeated cycles, another endothermic peak was observed around 570 K and it gradually became large with cycles (Fig.2). The appearance of this peak was closely associated with thermal treatment of the composites; thus the peak intensity increased with increasing pretreatment temperatures of 673-773 K. Since there were no DSC peaks under an atmosphere of helium, the newly emerged DSC peaks were derived from endothermically desorbed hydrogen [3].

When DSC for $(Mg/G)_{CH}$ was measured at 3 MPa or 6 MPa of hydrogen (Fig. 3), 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 ptake, respectively. The temperatures for H_2 uptake and release observed here were obviously lower than thermodynamic absorption and desorption temperatures for the 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. When the DSC traces were measured under a hydrogen atmosphere of 6 MPa, the peaks for H_2 uptake and release were shifted to higher temperatures. The H_2 uptake and release were clearly ascertained at 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 observed here is characterized by excellent reversibility and marked pressure dependence.

Unlike $(Mg/G)_{BN}$ and $(Mg/G)_{CH}$, the composites prepared without the additives did not show such hydrogen uptake and release other than those due to the formation and decomposition of MgH_2. The use of organic additives determines the degradation modes of graphite and the structural differences in decomposed graphite reflect the properties of H_2 uptake [2,3].

References

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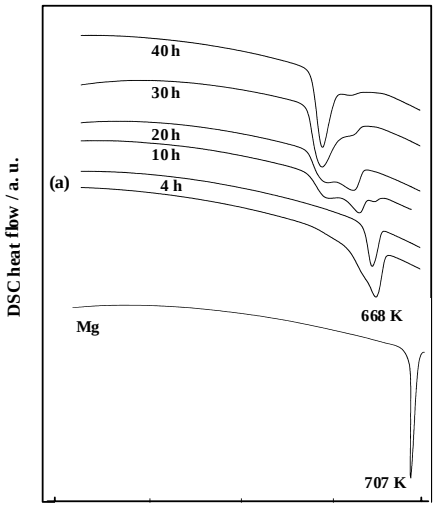
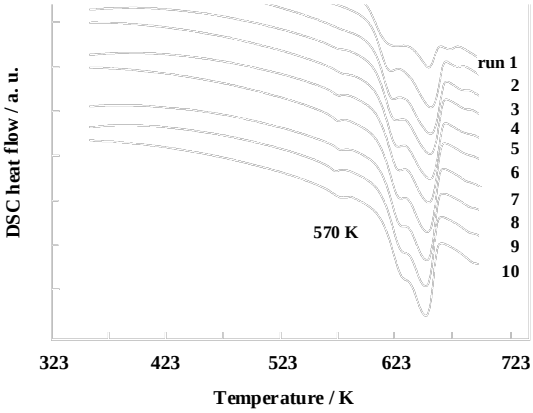


Fig. 1 DSC traces for various $(Mg/G)_{BN}$, $(Mg/G)_{none}$ and Mg samples. The $(Mg/G)_{BN}$ composites were prepared by grinding with benzene (8.0 cm^3) for (a) 4 h, (b) 10 h, (c) 20 h, (d) 30 h and (e) 40 h. $(Mg/G)_{none}$ was prepared by grinding without benzene for 15 h.

Fig.2 Repeated DSC measurements (run 1-10) on $(Mg/G)_{BN}$, prepared by grinding with benzene (8.0 cm^3) for 10 h.



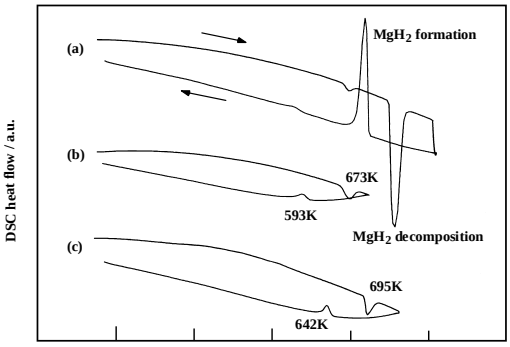


Fig. 3 DSC traces for $(Mg/G)_{CH}$, prepared by grinding with cyclohexane (15 cm^3) for 40 h. DSC was scanned (a) between 343 and 773 K under 3 MPa of H_2, (b) between 343 and 693 K under 3 MPa of H_2 and (c) between 343 and 733 K under 6 MPa of H_2