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# Magnesium-based Nanocomposites Synthesized by High-energy Ball Milling for Hydrogen Storage

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**Abstract**

Nanocrystalline $MgH_2$ obtained by ball milling with cyclohexane or benzene showed excellent properties for hydrogen storage. 1 at% Al-added nanocrystalline magnesium samples obtained by milling of $MgH_2$ with solutions of $Al(C_2H_5)_3$ in benzene showed the reversible hydrogen absorption/desorption cycles even at 0.1 MPa of hydrogen. Moreover, the hydrogen storage properties of magnesium hydride were markedly improved upon nanocomposite formation by ball milling of $MgH_2$ with Sn or SiC. For $MgH_2$/Sn and $MgH_2$/SiC nanocomposites, the dissociation temperature at 0.1 MPa of hydrogen was raised, compared to that for $MgH_2$.

## 1 Introduction

Magnesium and magnesium-containing systems (alloys and composites) are potential materials for hydrogen storage due to the high hydrogen storage capacity, the low cost and weight. However, their slow sorption kinetics and high thermodynamic stability of the hydride is a serious barrier to practical applications. Interest has recently centered on the topic of modifying the hydrogen storage properties of magnesium hydride.

In the present work the hydrogen storage properties of the nanocrystalline magnesium hydride obtained by ball milling of $MgH_2$ with cyclohexane or benzene are studied by X-ray diffraction (XRD), differential scanning calorimeter (DSC), thermal desorption spectrometry (TDS), thermogravimetry (TG) and pressure-composition isotherm (PCT) [1,2]. For nanocrystalline $MgH_2$ thus obtained, interesting features of the hydrogen desorption behavior are presented. For $MgH_2$/Sn [2,3] and $MgH_2$/SiC [4] nanocomposites we elucidate the hydrogen storage properties of magnesium hydride which are markedly improved upon ball milling of $MgH_2$ with Sn and SiC, respectively.

## 2 Experimental Procedure

$MgH_2$ (98 %), SiC and Sn (99.9 %) powders were purchased from Wako Pure Chemical Ind., Ltd. and Rare Metallic Co., Ltd., respectively. Cyclohexane and benzene used were reagent grade (>99.5%).

The preparation of nanocrystalline $MgH_2$ [1,2] and Mg-based nanocomposites ($MgH_2$/Sn [2,3] and $MgH_2$/SiC [4]) was carried out using a planetary-type ball mill (Kurimoto Ltd.; High G, BX 254), being capable of operating at a 863-rpm maximum speed. In a typical preparation of nanocrystalline $MgH_2$, $MgH_2$ (3.0 g) and cyclohexane (2.0 $cm^3$) were placed in a grinding bowl (coated with zirconia; cylindrical shape with volume of 160 $cm^3$) flushed thoroughly with dry nitrogen. The mixtures were subjected to ball milling with balls (zirconia; diameter 3 mm;

112 g) for 3 h. All operations concerning the magnesium samples were carried out without exposure to air.

The magnesium samples thus obtained were examined by XRD (Rigaku X-ray diffractometer, RINT 2200), DSC (TA Instruments Q10), TDS, TG (TA Instruments, TGA 2850 Thermogravimetric Analyzer) and PCT measurements (Suzuki Shokan Co. Ltd., PCT-1SDWIN).

## 3 Results and Discussion

### 3.1 Nanocrystalline $MgH_2$

In the hydrogen storage properties of nanocrystalline $MgH_2$ obtained by ball milling techniques, ball milling of $MgH_2$ with cyclohexane or benzene resulted in improvement of the absorption and desorption properties [1,2]. Interestingly, the desorption temperatures of the nanocrystalline $MgH_2$ were strongly dependent upon the rehydrogenation temperatures; the sample rehydrogenated at 290 K showed a lower desorption temperature by about 90 K than that rehydrogenated at 453 K [2]. Such a desorption behavior is associated with lattice defects such as dislocation and vacancy introduced during rehydrogenation.

Moreover, as shown in Figure.1, the reversible hydrogen absorption by 1 at% Al-added nanocrystalline $MgH_2$, obtained by milling of $MgH_2$ with solutions of $Al(C_2H_5)_3$ in benzene, was observed with a maximal capacity of 7.3 wt% even at a 0.1 MPa $H_2$ atmosphere [1].

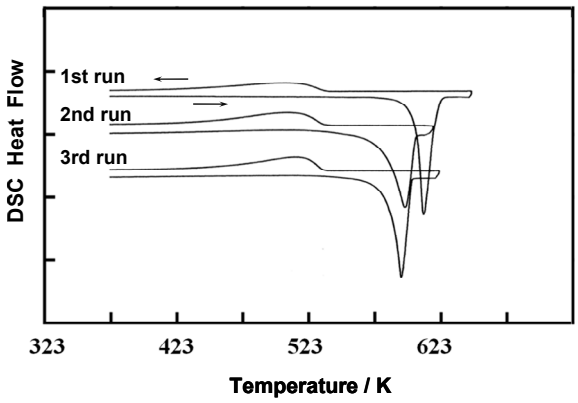


**Figure 1: DSC traces of 1 at% Al-added MgH2 obtained by ball milling of MgH2 with solutions of Al(C2H5)3 in benzene for 3 h.**

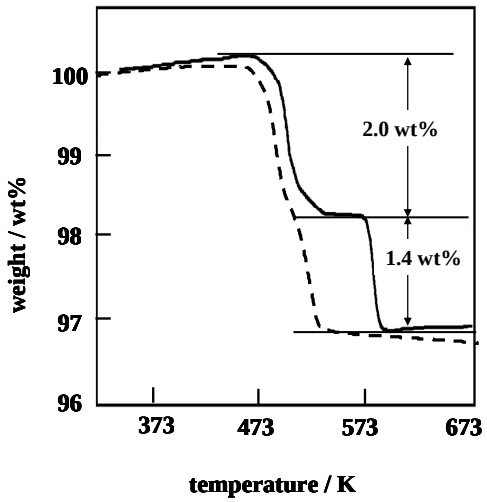


**Figure 2: TG of MgH2/Sn measured in a flow of hydrogen (solid line) or helium (dotted line) at 0.1 MPa.**

### 3.2 $MgH_2$/Sn and $MgH_2$/SiC nanocomposites

Upon ball milling of the nanocrystalline $MgH_2$ with Sn [2,3] or SiC [4], the properties of $MgH_2$ were further improved for hydrogen storage. TDS, TG, DSC and PCT measurements indicated the formation of $MgH_2$/Sn or $MgH_2$/SiC nanocomposites as a result of ball milling of $MgH_2$ with Sn or SiC, respectively, instead of a mere physical mixture.

As shown by TG measurements, the nanocomposite obtained when $MgH_2$ was ball-milled with 17 at% Sn contained two types of hydrogen species; the one was hydrogen (2.0 wt%) produced newly as a result of $MgH_2$/Sn nanocomposite formation and the other hydrogen (1.4 wt%) derived from $MgH_2$ remaining in $MgH_2$/Sn [3]. The properties of the $MgH_2$/Sn nanocomposite were further discussed in comparison with those of the physical mixture of $MgH_2$ and Sn [2].

Moreover, the hydrogen storage properties of $MgH_2$ were markedly modified upon ball milling with SiC [4]. The desorption temperatures of $MgH_2$/SiC tended to drop with increasing the composition of SiC (10-75 mol%) in the nanocomposites. The hydrogen desorption of $MgH_2$ as a starting material was observed around 705 K in TDS, while $MgH_2$ milled with 10 mol% SiC showed the desorption around 480 K. The hydrogen in $MgH_2$/SiC (75 mol%) was more destabilized, leading to lowering of the desorption temperature to about 437 K. XRD showed that in the nanocomposites with different compositions of SiC the magnesium constituent was highly dispersed in both the hydrogenation state and the dehydrogenation state. The hydrogen storage properties, especially desorption temperatures and thermodynamic parameters, were significantly improved as a result of nanocomposite formation by milling $MgH_2$ with 75 mol% SiC.

For $MgH_2$/SiC (75 mol%) obtained under different milling conditions, ball milling at 863 rpm for 0.5 h was fit to form the nanocomposites as shown in DSC traces (Figure. 3). In DSC measured under a 0.1 MPa hydrogen atmosphere, the two endothermic peaks assigned to dehydriding of $MgH_2$/SiC nanocomposites and $MgH_2$ remaining in $MgH_2$/SiC were observed around 520-570 K and 590-610 K, respectively. Taking into account the fact that the dissociation temperatures for the Mg-H system at 0.1 MPa hydrogen were about 560 K [5], the dehydriding temperature observed from 520 K was too low for $MgH_2$, indicating the formation of $MgH_2$/SiC nanocomposites. Ball milling at 650 rpm for 0.5 h was inadequate for the formation of nanocomposites; dehydriding of $MgH_2$ was exclusively observed around 590 K. In ball milling at 863 rpm for 0.5 h, the DSC peak corresponding to dehydriding of $MgH_2$ decreased, whereas that for the nanocomposites increased conversely.

PCT measurements of $MgH_2$/SiC (75 mol%) were carried out to evaluate further the properties of the hydrogen in the nanocomposites [4]. The sample was first subjected to the desorption isotherm measurements at 573 K with lowering hydrogen pressures from 10 MPa to 0.001 MPa, followed by pressurizing hydrogen to 10 MPa to measure the absorption isotherms. Finally the desorption isotherms were measured with the same procedures again. As shown in Figure. 4, the PCT traces obtained in the first desorption process were obviously different from that of $MgH_2$; the equilibrium pressures at 573 K were much higher than those predicted for $MgH_2$. This is consistent with the DSC results (Figure. 3) described previously. Thus $MgH_2$ was destabilized upon ball milling with SiC.

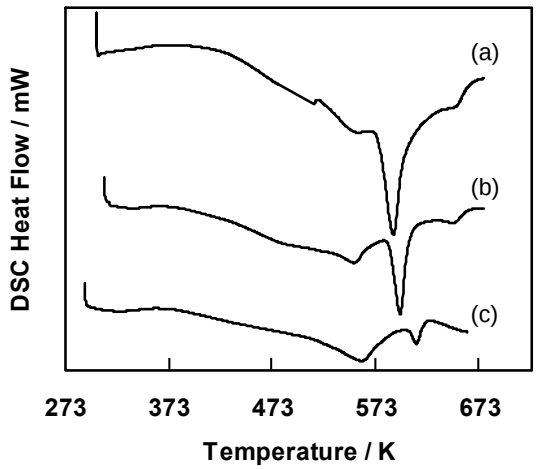


**Figure 3: DSC traces at 0.1 MPa of hydrogen for MaH2/SiC (75 mol%) prepared under different milling conditions: (a) 650 rpm, 0.5 h; (b) 863 rpm, 0.25 h; and (c) 863 rpm, 0.5 h.**

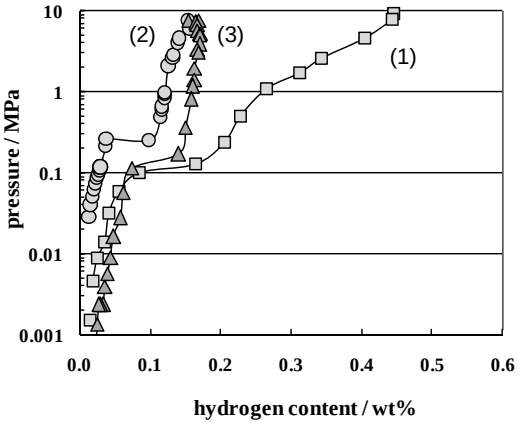


**Figure 4: Pressure-composition isotherms at 573 K for MgH2/SiC (75 mol%). Desorption/adsorption cycles, (1) → (2) → (3).**

However, the equilibrium pressures obtained for the following absorption (2) and desorption (3) processes at 573 K were very close to those of $MgH_2$. This indicates that the nanocomposites irreversibly broke down partly into magnesium and SiC at temperatures above 573 K. The absorption (2)/desorption (3) isotherms observed in Figure. 4 is probably attributed to the magnesium component generated after a breakdown at elevated temperatures.

For $MgH_2$/SiC nanocomposites, the reversibility of hydrogen absorption/desorption was certainly observed at lower temperatures.

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