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

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Abstract
Nanocrystalline MgH₂ 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 MgH₂ with solutions of Al(C₂H₅)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 MgH₂ with Sn or SiC. For MgH₂/Sn and MgH₂/SiC nanocomposites, the dissociation temperature at 0.1 MPa of hydrogen was raised, compared to that for MgH₂.

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 MgH₂ 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 MgH₂ thus obtained, interesting features of the hydrogen desorption behavior are presented. For MgH₂/Sn [2,3] and MgH₂/SiC [4] nanocomposites we elucidate the hydrogen storage properties of magnesium hydride which are markedly improved upon ball milling of MgH₂ with Sn and SiC, respectively.

2 Experimental Procedure
MgH₂ (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 MgH₂ [1,2] and Mg-based nanocomposites (MgH₂/Sn [2,3] and MgH₂/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 MgH₂, MgH₂ (3.0 g) and cyclohexane (2.0 cm³) were placed in a grinding bowl (coated with zirconia; cylindrical shape with volume of 160 cm³) 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$_2$H$_5$)$_3$ 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 MgH$_2$ obtained by ball milling of MgH$_2$ with solutions of Al(C$_2$H$_5$)$_3$ in benzene for 3 h.](image)

![Figure 2: TG of MgH$_2$/Sn measured in a flow of hydrogen (solid line) or helium (dotted line) at 0.1 MPa.](image)
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 MgH2. 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 MgH2/SiC nanocomposites, the reversibility of hydrogen absorption/desorption was certainly observed at lower temperatures.

References


