Preparation and Properties of Ball-Milled MgH2/Al Nanocomposites for Hydrogen Storage

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For reversible hydrogen storage properties of 17MgH2 + 12Al ↔ Mg17Al12 + 17H2, MgH2/Al nanocomposites (I)–(IV) synthesized by ball milling of MgH2 and Al (or AlH3) were studied in connection with milling conditions. The milling processes consisting of two steps were effective to improve the hydrogen storage behavior; MgH2 was first milled with solutions of triethylaluminum (TEA) in hexane, followed by addition of Al and TEA solutions. The mixtures were further milled to yield the nanocomposite (III). In preparing the nanocomposite (IV), AlH3 was used instead of Al. For the nanocomposites (III) and (IV), it was proved by XRD, TDS, DSC and PCI that such ball-milling led to high dispersion of nanocrystalline MgH2 in Al and/or AlH3 matrix in the resulting nanocomposites. In DSC measured under a 0.1 MPa hydrogen atmosphere, the nanocomposites (III) and (IV) exhibited reversible H2 absorption and desorption at 493–503 and 573–593 K, respectively.

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1. Introduction

Magnesium is a potential material for hydrogen storage due to its high storage capacity, low cost and weight. However, its slow kinetics and high thermodynamic stability of the hydride are barriers to practical applications. Many efforts have been done to improve its hydrogen storage properties. We have reported nanostructural magnesium: small particle size and high surface area are essential for fast kinetics.1,2) Moreover, Mg-based composite materials with other compounds (carbon,3) Nb2O5,4) complex hydride,5,6) etc.) or catalysts have been extensively studied. Alloysing a variety of elements has been also explored to improve the thermodynamic properties.7,8) A Mg–Al alloy for which better kinetics can be expected as well is one of interesting alloy systems.9) For samples of Mg–Al studied hitherto, arc melting and ball milling techniques have been commonly used to prepare the Mg–Al alloys. The use of ball milling arises from the fact that Mg has a low miscibility with other metals, a low melting temperature and a high vapor pressure.

In this study, ball milling of MgH2/Al to prepare nanocomposites rather than ball milling of Mg/Al to prepare alloys was adopted for sample preparation, and moreover the reversible hydrogen storage behavior of the resulting nanocomposites, MgH2/Al ↔ Mg17Al12 + H2, was studied by TDS, PCI and DSC. In the MgH2/Al nanocomposites, nanocrystalline MgH2 appears to function efficiently in the reaction with Al when highly dispersed in Al matrix, and consequently, the reversible hydrogen storage was found to occur under mild conditions: a 0.1 MPa hydrogen atmosphere.

In MgH2/Al systems so far studied, Glage et al.10) investigated a powder metallurgy approach for the production of a hydrogen storage MgH2/Al composite material. A systematic study of structural stability and dehydrogenation of (MgH2 + Al) powder mixtures was carried out by Shang et al.11) However, there have been few reports regarding the milling condition-dependent hydrogen storage properties for MgH2/Al nanocomposites. With the aim of destabilizing MgH2 we have previously studied MgH2/Sn nanocomposites, in which high dispersion of nanocrystalline MgH2 in Sn with subsequent destabilization reactions of the hydride through alloying with Sn results in improved hydrogen desorption characteristics.12,13) We therefore carried out further investigations on the hydrogen storage properties of MgH2/Al nanocomposites synthesized by ball milling of MgH2 and Al (or AlH3) in connection with milling conditions. Moreover, AlH3 was used instead of Al. AlH3 is considered brittle compared with Al. Thus the formation of nanocrystalline aluminum facilitates the subsequent destabilization reactions of MgH2 for reversible hydrogen storage. We herein report the details of this study.

2. Experimental Procedure

Al powders (99.9%) were purchased from Kojundo Chemical Laboratory Co., Ltd. MgH2 (98%) and triethylaluminum (TEA; 1 mol L\(^{-1}\) hexane solution) were obtained from Wako Pure Chemical Ind., Ltd. For AlH3, aluminum trihydride-diethyl etherate was synthesized by the reaction of AlCl3 with LiAlH4 in diethyl ether,14) followed by heating at around 333 K under vacuum to remove the solvating diethyl ether. It was confirmed by XRD that aluminum hydride thus prepared was \(\alpha\)-AlH3.15)

MgH2/Al nanocomposite materials were prepared using a planetary-type ball mill, as detailed in Ref. 12). In the preparation of samples, MgH2 of 3.5 g was always used, and Al (or AlH3) corresponding to Al/Mg ratio = 0.706 and TEA (4–8 mL) as an additive were added. The samples prepared under different milling conditions were referred to as nanocomposites (I)–(IV) as described later. The nanocomposites obtained were characterized by X-ray diffraction (XRD), thermal desorption spectrometry (TDS), differential scanning calorimeter (DSC) and pressure-compensation isotherm (PCI) according to the procedure previously reported.12)
3. Results and Discussions

3.1 Preparation of the MgH2/Al (I)–(III) and MgH2/AlH3 (IV) nanocomposites by different milling conditions

Ball milling of MgH2 with cyclohexane or benzene results in the formation of highly reactive nanocrystalline MgH2 with small crystallite sizes of 12–16 nm and high surface areas of 18–25 m² g⁻¹. Moreover, 1 at% Al-added nanocrystalline MgH2, obtained by milling MgH2 with solutions of TEA in hexane, has shown the reversible hydrogen storage with a maximal capacity of 7.3 mass% around 513–593 K in DSC measurements at 0.1 MPa. TEA exhibits a remarkable acceleration for hydrogen absorption/desorption properties of the nanocrystalline magnesium. TEA was therefore used in the preparation of the MgH2/Al and MgH2/AlH3 nanocomposites by ball milling as described below.

In a preparation of the MgH2/Al nanocomposite (I), MgH2 and Al were placed in a grinding bowl and milled together with cyclohexane for 20 h. The MgH2/Al nanocomposite (II) was prepared by ball milling of MgH2 and Al with solutions of TEA in hexane for 20 h. For the MgH2/Al nanocomposite (III), MgH2 was first milled with the TEA solutions for 5 h, followed by addition of Al and TEA solutions. The mixtures were further ball-milled for 15 h. The sample obtained when AlH3 was used instead of Al adopted in the preparation of the nanocomposite (III) was referred to as the MgH2/AlH3 nanocomposite (IV). Since AlH3 is far brittle compared with Al, ball milling is expected to progress more effectively. Moreover, the use of AlH3 would prevent to form the oxide or hydroxide layer on the surface. These are favorable for the formation of nanosized aluminum with smaller crystallites, leading to the formation of nanocomposite materials with improved hydrogen storage properties. The nanocomposites (I)–(IV) obtained thus are summarized in Table 1.

The preparation conditions of the nanocomposites strongly reflected differences in their surface areas. The surface areas of the samples (III) and (IV) were larger by an order of magnitude than that of the sample (I). As described previously, the first ball-milling of MgH2 with the organic additive results in the formation of nanocrystalline MgH2 with small crystallite sizes and high surface areas. Probably, this is closely associated with the formation of the nanocomposites (III) and (IV) by the subsequent milling processes with Al (or AlH3); MgH2 is used more efficiently for the nanocomposite formation when in a state of nanocrystalline.

3.2 Characterization of the nanocomposites (I)–(IV) by XRD

XRD of the nanocomposites (I)–(IV) as prepared is shown in Fig. 1 together with that of MgH2, Al and AlH3 as a starting material. The results were also shown in Table 1. It can first be seen from XRD (Fig. 1(I–IV)) that there were no additional diffraction peaks which suggested new phases, products or reactions resulting from ball milling of MgH2 and Al (or AlH3). Upon ball milling of MgH2/Al (I–III), the broadening of the diffraction peaks for MgH2 occurred, especially in the nanocomposite (III), but less markedly for Al. In XRD of (I) and (II), the two components of MgH2 and Al were similarly changed during ball milling and there were no marked differences between the samples. The nanocomposite (IV) showed broad diffraction peaks of MgH2 and Al besides, indicating that part of AlH3 was dehydrogenated to nanocrystalline Al during ball milling, owing to low desorption temperatures (ca. 373–403 K) of AlH3. For the nanocomposites (III) and (IV), ball milling resulted in remarkable broadening of diffraction peaks of MgH2; thus nanocrystalline MgH2 formed is presumed to be highly dispersed in Al and/or AlH3 matrix in the resulting nanocomposite materials. This is consistent with an increase in surface areas as shown in Table 1.

In each nanocomposite, the formation of γ-Mg17Al12 intermetallic compound was observed by the dehydrogenation when the samples were subjected to the evacuation treatment (2.6 × 10⁻² Pa; 1 h) at 543–573 K (Fig. 2). The formation of Mg17Al12 with cubic structures is considered to occur in two stages consisting of the successive reactions of (1) and (2).

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\begin{align*}
2\text{MgH}_2 + 3\text{Al} & \rightarrow \text{Mg}_2\text{Al}_3 + 2\text{H}_2 \\
9\text{MgH}_2 + 4\text{Mg}_2\text{Al}_3 & \rightarrow \text{Mg}_17\text{Al}_{12} + 9\text{H}_2
\end{align*}
\]
However, as shown in Fig. 2, XRD after the evacuation of the samples (I) and (II) at 573 K showed the existence of unreacted MgH$_2$ and/or Al in addition to the formation of Mg$_{17}$Al$_{12}$. Unlike the nanocomposites (III) and (IV), the samples (I) and (II) were not fully dehydrogenated at 573 K. This is consistent with the results of TDS (Fig. 3) as described in the next section. On the other hand, no diffraction peaks attributed to unreacted MgH$_2$, Mg and Al were observed in XRD (Fig. 2) of MgH$_2$/Al (III) and MgH$_2$/AlH$_3$ (IV) in spite of evacuation at a lower temperature (543 K) than 573 K. Thus complete dehydrogenation of (III) and (IV) to Mg$_{17}$Al$_{12}$ was found to efficiently occur even at 543 K, owing to the formation of nanocrystalline MgH$_2$ and Al (or AlH$_3$) in high dispersion by ball milling as shown above (Table 1 and Fig. 1). For MgH$_2$/AlH$_3$ (IV), the preferential dehydrogenation of AlH$_3$ to Al with the subsequent progress of reactions (1) and (2) during evacuation at elevated temperatures is predicted.

### 3.3 Hydrogen absorption/desorption properties of the nanocomposites (I)–(IV) by TDS, DSC and PCI

The hydrogen desorption properties of nanocrystalline MgH$_2$ in the nanocomposites (I)–(IV) were studied using TDS, which was measured under ca. 1.0 × 10$^{-2}$ Pa at a heating rate of 2.5 K min$^{-1}$ by continuously monitoring desorbed gases via quadrupolar mass spectrometer. Included in Fig. 3 for comparison are TDS traces of MgH$_2$ milled without additives; its desorption temperature of hydrogen was about 640 K. Upon ball milling of MgH$_2$ and Al (or AlH$_3$) with the TEA solutions, the desorption properties of the nanocrystalline MgH$_2$ were significantly improved. The onset temperature of hydrogen desorption for the nanocomposite (III) and (IV) fell to about 460 and 480 K, respectively. However, the desorption peak of (IV) observed around 370 K was assigned to the dehydrogenation of AlH$_3$ remaining in (IV). TDS traces of (III) obviously seem to contain two peaks at about 495 and 515 K, suggesting the occurrence of two continuous processes for hydrogen desorption from the MgH$_2$/Al nanocomposite. This probably corresponds to two endothermic peaks for hydrogen desorption in DSC traces (Fig. 4) shown later. Unlike MgH$_2$/Al (III), the desorption processes for MgH$_2$/Al (I) and (II) were not so much enhanced (Fig. 3). Especially, due to ball-milling without TEA and lower dispersion of the MgH$_2$ and Al components, low reactivity of MgH$_2$/Al (I) is presumed to be one of the factors behind broadening of TDS traces. These facts were well consistent with the XRD results (Figs. 1 and 2). Moreover, it is predicted that the formation of stable Mg–Al alloys according to the reactions (1) and (2) plays an important part as a driving force for the hydrogen desorption processes.

It was proved by DSC that the nanocomposites (III) and (IV) showed reversible H$_2$ absorption/desorption even at 0.1 MPa: an excellent reversibility of the successive reactions of (1) and (2). DSC measurements were made at a scanning rate of 2.0 K min$^{-1}$ under a 0.1 MPa hydrogen atmosphere. The samples were first subjected to the process of raising the temperature from 373–423 to 623–673 K, followed by lowering the temperature to make DSC measurements (a thick line in Fig. 4). Finally DSC was measured again with raising the temperature (a thin line). As shown in Fig. 4(a), when the temperature of the sample (I) was raised to 673 K, two endothermic DSC peaks were observed at around 600 and 650 K, namely owing to the dehydrogenation of MgH$_2$/Al and MgH$_2$ to Mg$_{17}$Al$_{12}$ and Mg, respectively. The
hydrogen desorption peak for unreacted MgH$_2$ remaining in the nanocomposite (I) appeared at around 650 K in DSC. This means incomplete dehydrogenation of (I), being consistent with XRD results (Fig. 2(a)) obtained after evacuation at 573 K. Subsequently, a broad exothermic peak by hydrogen absorption was observed with lowering the temperature. When the temperature was raised again, two similar endothermic peaks were observed, but more weakly. It is because the ball milling for MgH$_2$/Al (I) was not so successful in the formation of the nanocomposite that the reversibility of H$_2$ absorption/desorption rapidly failed in this way.

On the other hand, the nanocomposites (III) and (IV) were more excellent in reversible H$_2$ absorption/desorption. DSC traces of (III) and (IV) are shown in Figs. 4(b) and 4(c), respectively. In the first process of raising the temperature for (III), endothermic peaks split in two were observed. XRD of (III) collected at the temperatures (around 580 and 610 K) marked with an arrow in Fig. 4(b) showed the formation of Mg$_2$Al$_3$ and Mg$_{17}$Al$_{12}$, respectively, suggesting that the dehydrogenation reactions of (1) and (2) successively and completely occurred during raising the temperature. Because of rapid dehydrogenation reactions of (1) and (2) in the sample (IV), the two desorption processes were observed as a single endothermic peak in DSC (Fig. 4(c)). Moreover, unlike DSC traces of (I), there were no endothermic peaks derived from unreacted MgH$_2$ for the samples (III) and (IV). This is well consistent with XRD (Figs. 2(c) and 2(d)) after evacuation of (III) and (IV) at 543 K, respectively. DSC traces obtained during raising the temperature again were very similar to those for the first run. This indicates that the nanocomposites (III) and (IV) exhibit good reversibility of H$_2$ absorption/desorption within DSC operation conditions at 0.1 MPa.

To evaluate the thermodynamic properties of hydrogen in such nanocomposites, PCI measurements of MgH$_2$/Al (III) as a typical example were made (Fig. 5). After evacuating the nanocomposite (III) at 623 K to obtain Mg$_{17}$Al$_{12}$, the sample was first subjected to the absorption isotherm measurements at 623 K with pressurizing hydrogen from 0.001 to 10 MPa, followed by lowering hydrogen pressures to 0.001 MPa to measure the desorption isotherm. The PCI traces obtained in the first absorption process showed occurrence of the reaction of Mg$_{17}$Al$_{12}$ + 9H$_2$ → 9MgH$_2$ + 4Mg$_2$Al$_3$, followed by the reaction of Mg$_2$Al$_3$ + 2H$_2$ → 2MgH$_2$ + 3Al at a higher equilibrium pressure. The equilibrium pressures at 623 K for the hydrogen absorption of Mg$_{17}$Al$_{12}$ and Mg$_2$Al$_3$ were about 1.4–1.7 and 2.6–3 MPa, respectively. These are approximately equal to the values reported elsewhere. The desorption isotherm was similarly obtained in the reverse processes of the above reactions. Apparently, there was hysteresis between the absorption and desorption processes, and their equilibrium pressures in each process were within the values reported. No difference in the equilibrium pressure between the nanocomposites (III) and (IV) was observed.

4. Conclusion

In the study of the hydrogen storage properties of Mg$_{17}$Al$_{12}$, the use of the alloy or the MgH$_2$ + Al system as a sample seems to be of importance. We used here the latter sample in MgH$_2$/Al nanocomposite obtained by ball milling of MgH$_2$ with Al. The MgH$_2$/Al nanocomposites obtained by ball milling consisting of two steps exhibited reversible hydrogen storage behavior of MgH$_2$/Al ↔ Mg$_{17}$Al$_{12}$ + H$_2$ under mild conditions, probably due to high dispersion of nanocrystalline MgH$_2$ in Al matrix in the nanocomposite. Moreover, the nanocrystalline aluminum obtained when AlH$_3$ instead of Al was used facilitated the subsequent destabilization reactions of MgH$_2$ for reversible hydrogen storage.
REFERENCES