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Synthesis and hydrogen storage properties of mechanically ball-milled SiC/MgH_2 nanocomposites

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ABSTRACT

The hydrogen storage characteristics of SiC/MgH_2 nanocomposites which are prepared by mechanical ball milling of MgH_2 and SiC with cyclohexane have been studied. MgH_2 as a starting material exhibited a desorption peak of hydrogen at 705 K in thermal desorption spectrometry (TDS), while the ball-milled SiC/MgH_2 nanocomposites showed much lower desorption temperatures near 437 K. The hydrogen storage properties of SiC/MgH_2 were significantly improved as a result of nanocomposite formation. In addition, the nanocomposites were characterized by X-ray diffraction (XRD), thermogravimetry (TG), differential scanning calorimeter (DSC) and pressure–composition isotherm (PCT) measurements. For the SiC/MgH_2 nanocomposites, the reversibility of hydrogen absorption/desorption was observed, but heating above 573 K led to the irreversible breakdown of nanocomposites into MgH_2 and SiC.

1. Introduction

Developing highly efficient and safer means for hydrogen storage is one of key technologies to realize future hydrogen energy systems. Magnesium or magnesium-containing materials (alloys and composites) are considered as a promising candidate due to high hydrogen storage capacity (e.g. MgH_2: 7.6 wt.%; Mg_2NiH_4: 3.6 wt.%) [1–5]. However, these hydrides being thermodynamically very stable, a high operating temperature is required to obtain a significant hydrogen pressure for the desorption process. Their sluggish sorption kinetics for hydriding and dehydriding also prevents wide and practical use. Consequently, many attempts to eliminate these disadvantages of magnesium hydrides have been extensively studied from different standpoints of thermodynamics or kinetics.

Mechanical ball milling techniques are very often utilized to form nanostructured or nanocrystallized particles in expectation of promotion of the composite formation or improvement of kinetic properties. For mechanochemically prepared graphite/MgH_2 [6,7], graphite/Mg [8,9], carbon/MgH_2 [10], oxide/MgH_2 [11–13] and metal/MgH_2 [14,15], the hydrogen storage characteristics have been studied. It has been shown that Nb_2O_5/MgH_2 upon mechanical milling is kinetically activated for hydriding and dehydriding processes [16–18]. Destabilizing of the hydride by alloy or compound formation in dehydrogenated state has been examined to overcome the thermodynamic constraints [19–21]. We have shown that the Sn/MgH_2 formed by ball milling of MgH_2 with Sn results in thermodynamic destabilization of the hydride, lowering the dehydrogenation temperature [22].

It has been recently found for SiC/MgH_2 nanocomposites prepared by mechanical milling of MgH_2 and SiC that SiC significantly improves the performance of MgH_2 for hydrogen storage [23]. Guo et al. [24] also reported the effects of the addition of SiC on the hydrogen storage properties of MgH_2 synthesized by ball milling. In this paper, Destabilization of magnesium hydride was observed upon ball milling with SiC, resulting in lowering of dehydrogenation temperatures below 437 K in TDS. We also discussed how various duration of ball milling of MgH_2 with different concentration of SiC affected the hydrogen storage characteristics. In addition, the reversibility of hydrogen storage for the SiC/MgH_2 nanocomposite has been studied using PCT. The findings obtained here would be useful and significant for developing potential hydrogen storage systems in future.

2. Experimental

Magnesium hydride (MgH_2: 98%) and silicon carbide (SiC) powders were purchased from Wako Pure Chemicals Co., Ltd. Cyclohexane was of research purity. The sample preparation was carried out with a planetary-type ball mill (High G: BX 254; Kurimoto Ltd.) using a grinding bowl (coated with zirconia; cylindrical shape with volume of 160 cm^3) and zirconia balls (size: 3 mm in diameter). In a typical preparation of the 22 mol.% SiC/MgH_2 nanocomposite, MgH_2 (4.2 g) and SiC (1.8 g) were placed in the grinding bowl (ratio of balls to powders: 37/1) and were subjected to ball milling (863 rpm) with cyclohexane (8 cm^3) as an additive for 5 h. We have

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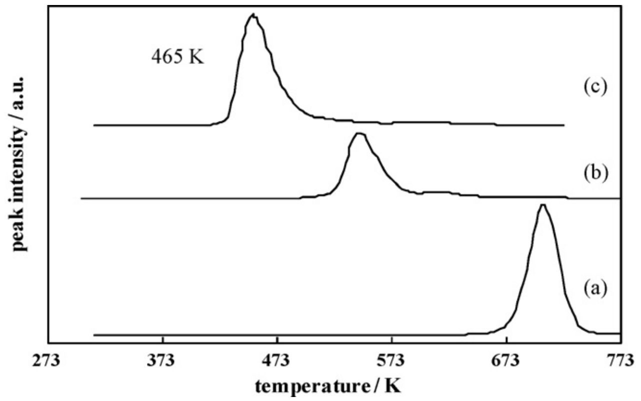


Fig. 1. TDS of various MgH_2 samples: (a) MgH_2 (starting material), (b) MgH_2 milled with cyclohexane and (c) 22 mol.% SiC/MgH_2 nanocomposite obtained by ball milling with cyclohexane.

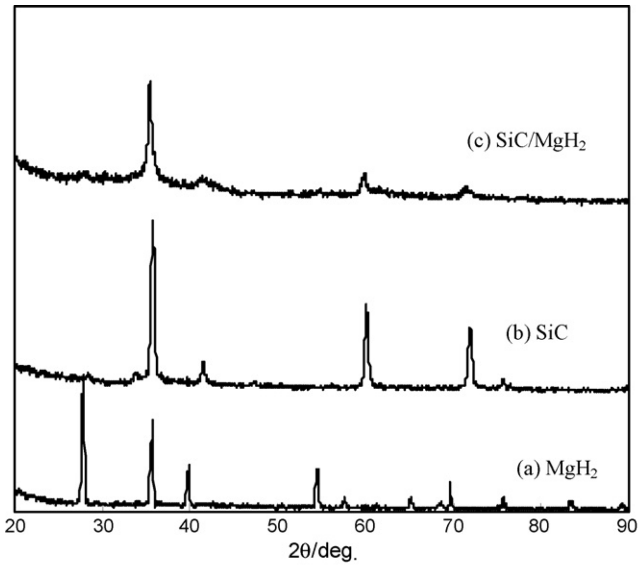


Fig. 2. XRD of (a) MgH_2 (starting material), (b) SiC (starting material) and (c) 22 mol.% SiC/MgH_2 nanocomposite obtained by ball milling with cyclohexane.

proposed that the use of organic additives, such as cyclohexane, in the milling process is crucial in enhancing the stability and dispersion of nanocrystallized magnesium particles [25].

The properties of hydrogen in SiC/MgH_2 were evaluated by differential scanning calorimeter (DSC; TA Instruments Q10) under an atmosphere (0.1 MPa) of hydrogen or argon. Thermal desorption spectrometry (TDS) measurements were made *in vacuo* at a heating rate of 2 K/min by continuously monitoring desorbed gases *via* quadrupolar mass spectrometer. Thermogravimetry (TG) was made on a TA Instruments TGA 2850 Thermogravimetric Analyzer under an argon atmosphere (0.1 MPa). The nanocomposite was collected on a sample pan, hermetically sealed by a sample encapsulating press and transferred to the TG sample chamber. PCT traces (PCT-1SDWIN; Suzuki Shokan Co., Ltd.) were measured at 573 K in the range of 0.001–10 MPa. All operations concerning the nanocomposite samples were carried out without exposure to air.

3. Results and discussion

3.1. Nanocomposites prepared by ball milling of MgH_2 and SiC with cyclohexane

As shown in TDS of Fig. 1, MgH_2 as a starting material exhibited a desorption peak of hydrogen at 705 K. MgH_2 showed much lower desorption temperatures near 540 K when ball-milled with cyclohexane. The ball milling technique is an effective way of activating magnesium with nanostructures and forming nanocomposites for hydrogen storage [22,23,25]. Moreover, the organic additive such as cyclohexane promotes the dispersion of the nanocrystalline MgH_2 particles during ball milling, resulting in the formation of highly reactive MgH_2 with small crystallite sizes of about 12 nm and high surface areas of 18 m^2/g [25]. When 22 mol.% SiC was added to MgH_2, followed by ball milling with cyclohexane for 5 h, the dehydrogenation temperature of the products obtained fell greatly as shown in Fig. 1(c). The SiC/MgH_2 nanocomposite, thus, prepared showed much lower dehydrogenation temperatures near 465 K. This is superior to the results on mechanically milled Sn/MgH_2 [22] and Nb_2O_5/MgH_2 nanocomposites [17]. For Sn/MgH_2, it is proved by TG and DSC measurements that the nanocomposite formation of MgH_2 with Sn results in thermodynamic destabilization of the hydride, lowering the dehydrogenation temperature to 490 K [22]. On the other hand, it has been shown for the ball-milled Nb_2O_5/MgH_2 that the kinetic properties of hydrogenation and dehydrogenation are significantly enhanced. Hanada et al. report that Nb oxide exerts the catalytic effect for the hydrogen desorption processes and that the most of hydrogen is desorbed in the temperature range from 473 K to 523 K [16,17].

XRD of the 22 mol.% SiC/MgH_2 sample which exhibited the TDS traces in Fig. 1(c), is shown in Fig. 2 in comparison with that of the constituents (MgH_2 and SiC). There were no additional diffraction peaks corresponding to new crystalline phases or products formed as a result of ball milling of MgH_2 and SiC. It has been shown that Mg_2Si with cubic structures is readily formed by alloying of Mg with Si in powder metallurgy [26], but no formation of Mg_2Si was observed here. As shown in Fig. 2(c), the diffraction peaks of the host MgH_2 were hardly observed, while SiC showed the broadening of the peaks to some extent. This indicates that the MgH_2 particles in the resulting nanocomposite are highly dispersed in a nanocrytalline state, probably leading to lowering the dehydrogenation temperatures as shown in Fig. 1. Ball milling of MgH_2 and SiC resulted in the formation of the nanocomposites with highly dispersed MgH_2 in intimate contact with SiC particles, which further showed interesting properties of hydrogen storage as described later.

3.2. Influence of ball milling conditions on characteristics of SiC/MgH_2 nanocomposites

The properties of SiC/MgH_2 for hydrogen storage were significantly influenced by the ball milling conditions for preparation of the nanocomposites. As shown in Fig. 3, the dehydrogenation

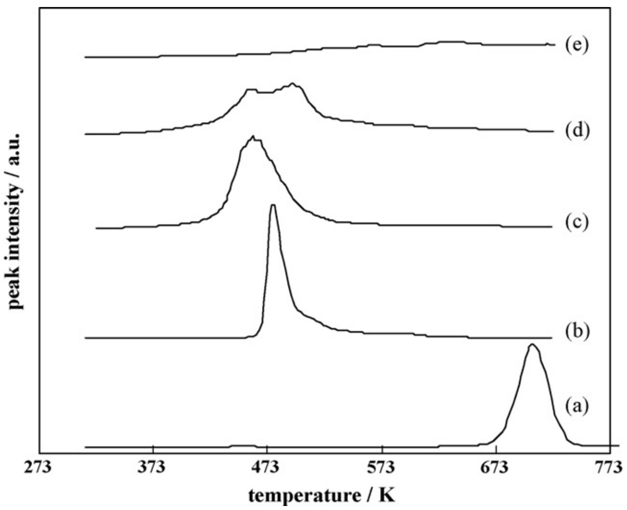


Fig. 3. TDS of SiC/MgH_2 nanocomposites with different composition of SiC; (a) 0 mol.%, (b) 10 mol.%, (c) 22 mol.%, (d) 62 mol.% and (e) 75 mol.%.

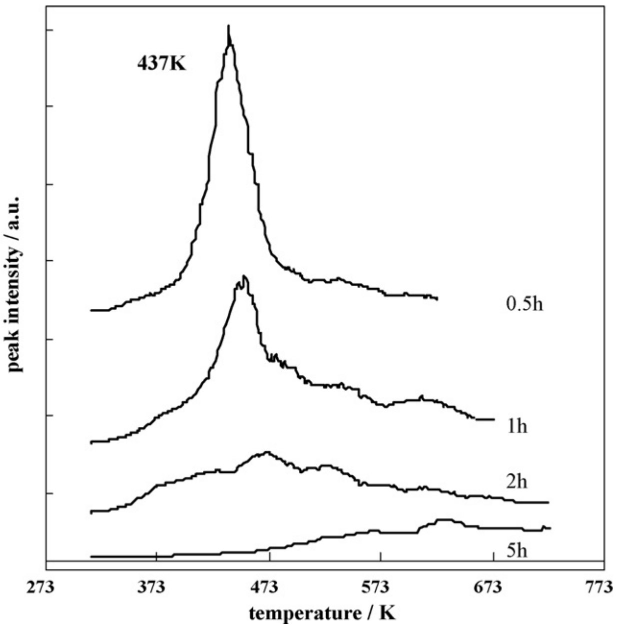


Fig. 4. TDS of 75 mol.% SiC/MgH_2 prepared with different milling times (0.5 h, 1 h, 2 h and 5 h).

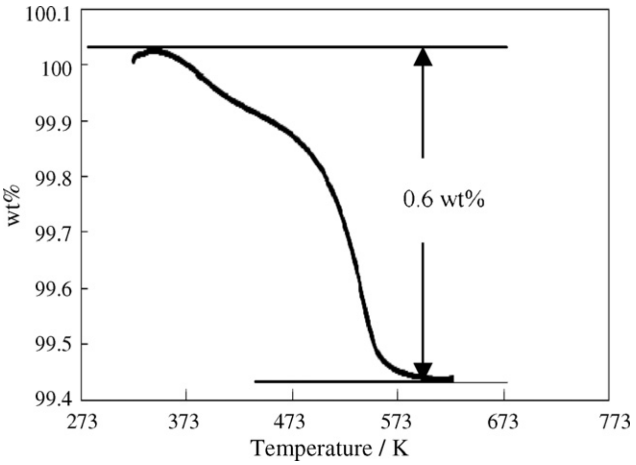


Fig. 5. TG of 75 mol.% SiC/MgH_2 prepared by ball milling for 0.5 h.

temperatures from SiC/MgH_2 showed a tendency to drop with increasing the composition of SiC (10–75 mol.%) in the nanocomposites. The dehydrogenation of 10 mol.% SiC/MgH_2 was observed around 480 K, whereas the hydrogen in 62 mol.% SiC/MgH_2 was more destabilized, leading to lowering of the dehydrogenation temperature to about 460 K. Moreover, the shape of TDS peaks of hydrogen simultaneously broadened with increasing the composition of SiC. For the nanocomposite with 75 mol.% SiC, the desorption peak of hydrogen was hardly observed over the temperature 300 to 773 K. Thus, upon ball milling of MgH_2 and SiC the hydride is destabilized, resulting in lowering the desorption temperatures to a considerable extent, and consequently, most of the hydrogen in the nanocomposite is considered to be released during ball milling.

To confirm that hydrogen was released during the ball milling process, the ball milling time for the preparation of 75 mol.% SiC/MgH_2 was shortened from 5 h to 0.5 h. As shown in Fig. 4, the magnitude of H_2 desorption peaks in TDS increased with shortening a period of milling for preparation and the samples obtained by milling for 0.5 h showed TDS traces of hydrogen around 437 K. The onset of the dehydrogenation of the nanocomposites began below 373 K. This indicates the existence of remaining hydrogen in the sample which is not released, due to shortening of the milling time. The amount of the remaining hydrogen in 75 mol.% SiC/MgH_2 was estimated by thermogravimetry to be 0.6 wt.% (Fig. 5). Since the theoretical amounts of hydrogen contained in 75 mol.% SiC/MgH_2 are about 1.4 wt.%, this means that about 60% of the hydrogen in SiC/MgH_2 was released during ball milling. As shown in Fig. 5, a loss in weight began from about 350 K and was completed around 570 K. Since cyclohexane used in ball milling of 75 mol.% SiC/MgH_2 and other volatile components were hardly detected in TDS measurements in the range of temperatures above 350 K, there was a quite agreement between the results of TDS (Fig. 4) and TG (Fig. 5) with changes in temperature.

As shown in Fig. 6, XRD of 75 mol.% SiC/MgH_2 was hardly changed when the milling time was reduced from 5 h to 0.5 h. Moreover, the diffraction peaks corresponding to a dehydrogenated state, such as metallic magnesium, were not observed in XRD of the sample after being milled for 5 h. The metallic phase of magnesium was not observed in XRD (Fig. 6(c)) when the nanocomposite ball-milled for 0.5 h was dehydrogenated upon evacuation. Thus, the magnesium constituent appears to be highly dispersed in the nanocomposite both in hydrogenation and in dehydrogenation.

50 mol.% SiC/MgH_2 and 22 mol.% SiC/MgH_2 showed hydrogen release of 60% and 32% during ball milling for the theoretical amounts of 3.0 wt.% and 5.3 wt.%, respectively. This is consistent with the results of TDS and the proportion of hydrogen released during ball milling increased with increasing the composition of SiC in the nanocomposite.

It has been shown by Vajo et al. [27,28] that for the Si/MgH_2 system, destabilization of MgH_2 by the formation of Mg_2Si in the dehydrogenated state is expected according to reaction shown as follows:

$$2MgH_2 + Si \rightarrow Mg_2Si + 2H_2.$$

MgH_2 is destabilized by the addition of Si, resulting in a dramatic decrease in dehydrogenation temperatures. The formation of Mg_2Si as a stable alloy upon dehydrogenation is driving forces for the reaction, but the rehydrogenation of Si/MgH_2 is not accomplished due to negligible reactivity of Mg_2Si toward hydrogen [27,29]. As shown in XRD of the SiC/MgH_2 system (Figs. 2(c), 6(a) and (b)), the formation of Mg_2Si phase was not detected at all for the samples with all compositions of SiC (10–75 mol.%) studied. Moreover, no formation of Mg_2Si was observed after the dehydrogenation of SiC/MgH_2 nanocomposites (Fig. 6(c)). Thus, the drop in dehydrogenation temperatures observed for the SiC/MgH_2 system is not the case for the

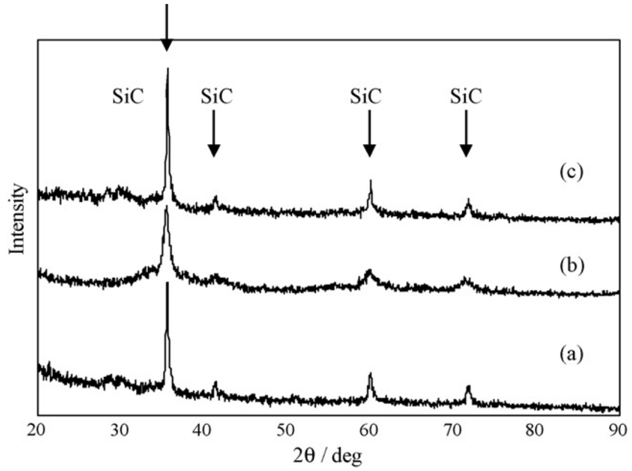


Fig. 6. XRD of 75 mol.% SiC/MgH_2 prepared by ball milling for (a) 0.5 h and (b) 5 h, and (c) XRD of 0.5 h milled 75 mol.% SiC/MgH_2 after dehydrogenation.

Si/MgH_2 system [27,28]. SiC probably plays several important roles in the SiC/MgH_2 nanocomposites. The addition of SiC helps to break up MgH_2 particles and reduce the grain size, thereby achieving high dispersion of MgH_2 in the nanocomposite. This kinetically enhances the sorption processes of hydrogen. For the SiC/MgH_2 system by Guo [24], similar effects are observed although there is a difference in quantity of SiC added.

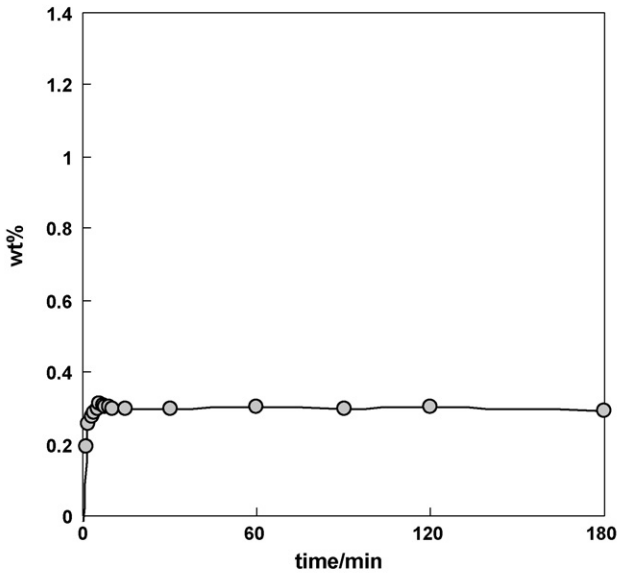


Fig. 7. Time courses of the rehydrogenation at 453 K after the dehydrogenation of 75 mol.% SiC/MgH_2.

As shown so far, the nanocomposites with 75 mol.% SiC gave excellent results. This further implies that MgH_2 are used more efficiently when highly dispersed in SiC particles over a certain concentration. However, 75 mol.% SiC/MgH_2 examined here is not practical in hydrogen capacity (wt.%); therefore minimizing SiC used becomes an important aspect in future.

3.3. *Reversibility of dehydrogenation/rehydrogenation*

The reversibility of dehydrogenation/rehydrogenation of SiC/MgH_2 was examined. To remove the hydrogen (0.6 wt.%) remaining in 75 mol.% SiC/MgH_2 milled for 0.5 h, the sample was heated to 493 K, followed by contact with hydrogen of 0.0667 MPa at 453 K. As shown by the time courses of rehydrogenation (Fig. 7), the sample quickly absorbed hydrogen corresponding to 0.3 wt.% even under such mild conditions. TDS (Fig. 8) of the sample, thus, rehydrogenated showed that the hydrogen reversibly absorbed in the nanocomposite.

PCT measurements of 75 mol.% SiC/MgH_2 were additionally carried out to evaluate the properties of the hydrogen in the nanocomposite (Fig. 9). 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 again. As shown in Fig. 9, the PCT traces obtained in the first desorption process was obviously different from that of MgH_2; the equilibrium pressures at 573 K were much higher than those predicted for MgH_2 [30,31]. MgH_2 was destabilized by ball milling with SiC. The amounts of desorbed hydrogen were about 0.45 wt.%, which was approximately equal to that estimated by TG shown in Fig. 5. However, the equilibrium pressures obtained for the following absorption and desorption processes at 573 K were very close to those of MgH_2 [30,31]. The amounts of hydrogen absorbed and desorbed were reduced to one-half its initial value. These facts suggest that the nanocomposites irreversibly broke down partly into magnesium and SiC, and partly into unknowns during repeated runs, perhaps due to measurements at elevated temperatures.

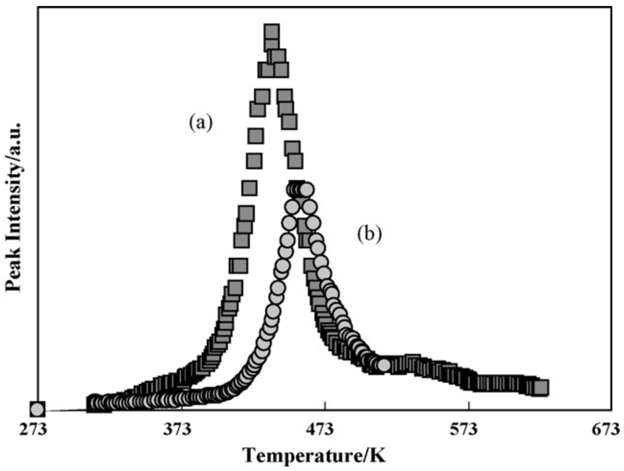


Fig. 8. TDS of the rehydrogenated nanocomposite sample; (a) as prepared and (b) rehydrogenated sample.

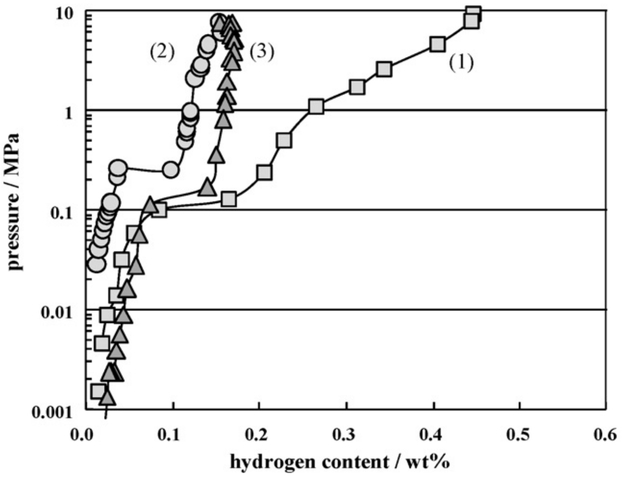
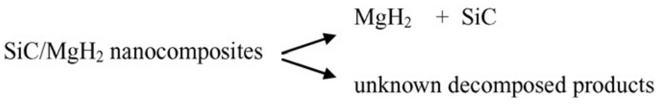


Fig. 9. Pressure–composition isotherms measured at 573 K for 75 mol.% SiC/MgH_2. Desorption/absorption cycles; (1) → (2) → (3).



The absorption (○)/desorption (Δ) isotherms observed in Fig. 9 is probably attributed to the magnesium component generated after a breakdown at elevated temperatures.

4. Conclusion

The synthesis of hydrogen storage materials by ball milling of MgH_2 and SiC has been studied. The hydrogen storage properties of MgH_2 were markedly modified upon ball milling with SiC. The dehydrogenation temperatures of SiC/MgH_2 tended to drop with increasing the composition of SiC (10–75 mol.%) in the nanocomposites. The dehydrogenation of 10 mol.% SiC/MgH_2 was observed around 480 K in TDS, while the hydrogen in 75 mol.% SiC/MgH_2 was more destabilized, leading to lowering of the dehydrogenation 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 dehydrogenation temperatures and thermodynamic parameters, were significantly improved as a result of nanocomposite formation by milling MgH_2 with 75 mol.% SiC. PCT measurements of 75 mol.% SiC/MgH_2 exhibited occurrence of hydride destabilization; the equilibrium pressures at 573 K were much higher than the values predicted for MgH_2. For the SiC/MgH_2 nanocomposites the reversibility of hydrogenation/dehydrogenation was observed. However, the nanocomposites irreversibly broke down partly into MgH_2 and SiC at temperatures above 573 K.

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