Reversible hydrogen-storage properties of Mg-Ti hydrides prepared by GPa hydrogen pressure and mechanical alloying

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Abstract

A ternary hydride, the face-centered cubic (FCC) type Mg_7TiH_{16}, synthesized under 8 GPa hydrogen pressure (HP) exhibited a reversible hydrogenation and dehydrogenation property around 600K on the differential scanning calorimeter (DSC) measurements. The FCC phase was decomposed during hydrogen releasing and restoring cycles. After the hydrogen restored process, the XRD pattern consisted of MgH_2, TiH_2 and Mg peaks. Meanwhile, a mechanically-alloyed (MA) $7MgH_2+TiH_2$ sample exhibited similar hydrogen storage properties to the HP sample. Based on a structural analysis using the synchrotron XRD data, it was shown that the phase abundance for the HP sample is equivalent to the one for the MA sample.

1. Introduction

Hydrogen is a clean energy source alternating fossil fuel. However, large volumes are necessary to store gaseous hydrogen. Hydrogen storage material is one of the ways to realize a compact and safe hydrogen storage system. The important requirements for hydrogen storage materials are high hydrogen capacity and reversible hydrogen storage properties. In order to apply the hydrogen storage materials to fuel cell vehicles, low releasing temperature (< 423 K) is required.

A lot of attention has been paid to magnesium hydride (MgH_2) as a promising candidate of hydrogen storage materials because of its high hydrogen storage capacity of 7.6 wt%. However, the hydrogen restoring reaction is very slow, and this material demands high temperatures above 700 K (Stampfer et al., 1960). These shortcomings have to be improved for practical use.

In order to improve the reaction kinetics without significantly reducing the advantageous storage properties, adding other metals to MgH_2 has been carried out. The Mg_2TH_x (T = Ni, Fe, Co; x = 4 - 6) (Reilly and Wiswall, 1968; Didisheim et al, 1984; Zolliker et al., 1985) are classical examples. In these cases, the Mg does not form any intermetallic alloys with Fe and Co. The hydrogen is essential for maintaining the Mg_2FeH_6 and Mg_2CoH_5 structures. These results suggest that a metal atom structure stabilized by hydrogen would provide a beneficial influence on lowering the dehydrogenation temperature (Reilly and Wiswall, 1968).

Various new Mg-based hydrides, such as the Mg_3MnH_7 (Bortz et al., 1998), $Mg_3MnH_{~6}$ (Blomqvist et al., 2003), Mg_3CrH_6 (Kyoi et al., 2003; Rönnebro et al., 2004) and Mg-RE-H phases

(RE: rare earth elements) (Kamegawa et al., 2006) were created using high pressure (HP) techniques. Furthermore, a series of face centered cubic (FCC) type Mg-rich hydrides, Mg_7MH_x (M = Sc, Ti, V, Zr, Nb, Hf and Ta), were synthesized by high 8GPa hydrogen pressure (Kyoi et al., 2004a; 2004b; Rönnebro et al., 2005; Sato et al., 2006; Kyoi et al., 2007; Kyoi et al., 2008a; 2008b; Takasaki et al., 2007a; 2007b; 2013). These materials release 4-7 wt.% hydrogen at 523-650 K, being lower by 70-190 K than that of MgH_2. In particular, the Mg_7TiH_x exhibited higher hydrogen releasing capacity and lower releasing temperature than the other Mg_7MH_x. The lighter atomic weight of Ti is the reason for higher capacity.

Mechanical alloying (MA) is known as a popular method to improve the hydrogen kinetics of MgH_2 (Song et al., 1995; Gross et al., 1996). This method is attributed to a high density of defects and grain boundaries in the nanocrystalline hydride. Adding transition metals during the ball milling with magnesium leads to a better performance. Mg-transition metal (M) binary alloy and Mg-M-H ternary hydrides were recently synthesized not only by thin-film (Vermeulen et al., 2006), but also by the MA technique (Asano and Akiba, 2009; Asano et al., 2009).

In this study, the hydrogen storage properties of the HP synthesized FCC Mg_7TiH_x phases was investigated by comparison with the MA treated $7MgH_2+TiH_2$ samples. In order to investigate the reversible hydrogen capabilities of these Mg-Ti-H materials, structural analyses using synchrotron X-ray diffraction measurements were carried out.

2. Experimental procedure

2.1 GPa high-pressure (HP) synthesis (Fukai and Okuma, 1993)

A commercially available powder of MgH_2 (Aldrich Chemical Co., purity 90 %, containing Mg as a major impurity) and

TiH$_2$ (High Purity Chemicals Co., purity 99 %) were used as the starting material. The powders of the binary hydrides were mixed at a molar ratio (MgH$_2$: TiH$_2$ = 7 : 1), and then pressed into pellets in a glove box filled with Ar. Pellets composed of NaBH$_4$ (Aldrich Chemical Co., purity 98 %) and Ca(OH)$_2$ (Wako Pure Chemical Industries, Ltd., purity 99.9 %) were also prepared for use as an internal hydrogen source. The pellet composed of MgH$_2$ and TiH$_2$ was sandwiched between BN thin discs, placed between the pellets of the hydrogen source, then sealed in a NaCl capsule. The capsule was surrounded by a carbon heater, which was placed at the center of a pyrophyllite octahedral cell. Details of this setup are illustrated in previous reports (Kyoi et al., 2003; Rönnebro et al., 2005). The octahedral cell was compressed to the desired pressure (8 GPa) in 6-8 multianvils using an ultra-high pressure generating apparatus (Sumitomo Heavy Industries, Ltd., UHP-2000). The sample mixtures were subsequently heated at about 17 K/min and up to 873 K. The temperature was held for 1 h at the desired pressure, where a sufficient amount of hydrogen was supplied from the hydrogen source into the sample space.

2.2 Mechanical alloying (MA)

In this procedure, the reagent powders (MgH$_2$ and TiH$_2$) are equivalent to those of the HP synthesis. The powder mixture (MgH$_2$: TiH$_2$ = 7 : 1) was poured into a steel container together with 5 mmφ stainless balls. The balls to powder weight ratio was 30 : 1. The container was sealed in an Ar filled glove box, then 0.5MPa hydrogen gas was introduced into it. The mixture was mechanically milled for 5 hours at 400 rpm using a planetary ball milling apparatus (FRITSCH P-7).

2.3 Characterizations

The phase component in the resultant specimen was charactarized by diffraction patterns using the synchrotron radiation facility SPring-8, Japan, at beam line BL19B2. A large Debye-Scherrer camera was installed in order to detect the fine powder diffraction patterns. The wavelength was calibrated to λ = 0.7 Å or 0.75 Å using CeO$_2$ as the standard. The X-ray exposure time was 5 min for each sample. The sample powders were contained in glass capillaries (D = 0.3 mm) and sealed with glue in an argon filled glove box to prevent contamination. The structural refinements were made using the Rietveld program RIETAN-2000 (Izumi and Ikeda, 2003). The hydrogen desorption and absorption properties were measured by DSC apparatus (Rigaku DSC8230HP) at the heating rate of 10 K/min with an H2 pressure of 0.1 MPa.

3. Results and discussion

3.1 Structure and hydrogen storage behaviors of HP and MA samples

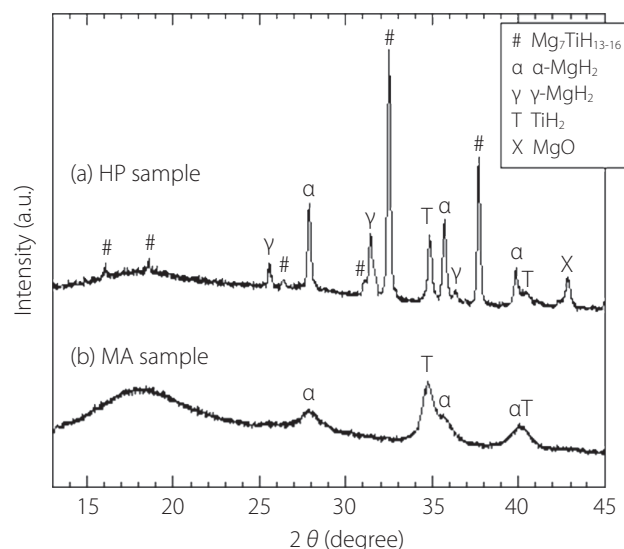Figure 1(a) shows the XRD patterns of the high-pressure

Figure 1: X-ray diffraction patterns with Cu-Kα radiation for the (a) HP and (b) MA Mg-Ti hydride samples

synthesized (HP) sample containing the face-centered cubic (fcc)-type Mg$_7$TiH$_{16}$ (Kyoi et al., 2004a; Rönnebro et al., 2005) and unreacted materials, such as α-MgH$_2$, MH$_x$, and MgO impurity. Small peaks due to the Ca$_7$Ge-type super-lattice structure were observed. According to reference of Vajeeston et al., 2006, the MgH$_2$ structure is transformed to an fcc-type one at 9 GPa pressure. However, the fcc structure returns to the original bcc-like structure (α-MgH$_2$) when the pressure is released. Introducing the fcc-type TiH$_2$ into the MgH$_2$ lattice would stabilize the fcc-type MgH$_2$ and the Mg$_7$TiH$_{16}$ phase was maintained even after the pressure release.

Figure 1(b) shows the XRD patterns for the mechanically alloyed (MA) 7MgH$_2$ + TiH$_2$ sample, consisting of broadened MgH$_2$ and TiH$_2$ patterns. The broadened peak structures would be ascribed to the strains or defects due to the MA treatment. This pattern is equivalent to the MA-treated nMgH$_2$ + TiH$_2$ samples (n = 4, 7) reported by other groups (Asano and Akiba, 2009; Choi et al., 2008). Meanwhile, the fcc-type Mg-Ti-H phase was formed by the MA treatment of MgH$_2$: Ti = 1 : 1 (Asano and Akiba, 2009).

Figure 2 shows the DSC data of the HP and MA samples observed in a 0.1MPa hydrogen atmosphere. During the heating step (labeled by arrows (I)-(III)), an endothermic peak for the hydrogen release was observed around 600 K. During the cooling step (arrows (IV)-(VI)), an exothermic peak for the hydrogen restoration was detected around 550 K. For the HP sample (solid line), the raw DSC data was divided by the mass fraction of the Mg$_7$TiH$_{16}$ phase (36 wt.%) (Takasaki et al., 2008). This peak area is almost equivalent to that of the MA sample (dashed line), suggesting that the reversible hydrogen storage capacity of the HP sample originates from the Mg$_7$TiH$_{16}$ phase.
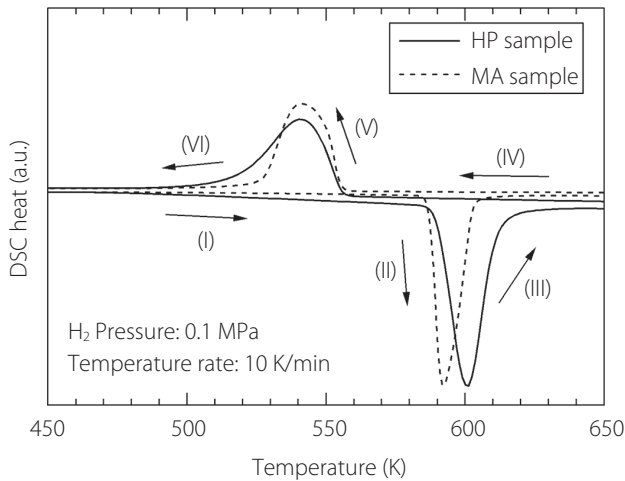
Figure 2: DSC curves for the HP (solid curve) and MA (dashed curve) Mg-Ti hydride samples under 0.1 MPa hydrogen pressure at the heating and cooling rate of 10 K/min

3.2 Phase abundance of HP and MA samples after hydrogen cycles

Figure 3 shows the synchrotron XRD pattern and the Rietveld refinement for the HP sample after the hydrogen releasing and restoring process. The Ca$_7$Ge-type fcc peaks disappeared and the diffraction peaks were indexed to α-MgH$_2$, Mg, TiH$_2$ and MgO, suggesting that the ordered Mg$_7$TiH$_{16}$ structure is decomposed to the MgH$_2$, Mg and TiH$_2$ phases. Meanwhile, the reversible hydrogen storage property was maintained even after the decomposition as shown in Figure 2. This characteristic is very different from the hydrogenation properties of MgH$_2$, TiH$_2$ and their initial mixture (Kyoi et al., 2004a).

Figure 4 shows the XRD pattern for the MA sample after the hydrogen cycles. The phase composition is equivalent to that of the HP sample in Figure 3. The MgH$_2$ and Mg peaks have become sharper than the MgH$_2$ peaks before the hydrogen cycles. Figure 5 shows the phase abundances for both sam-
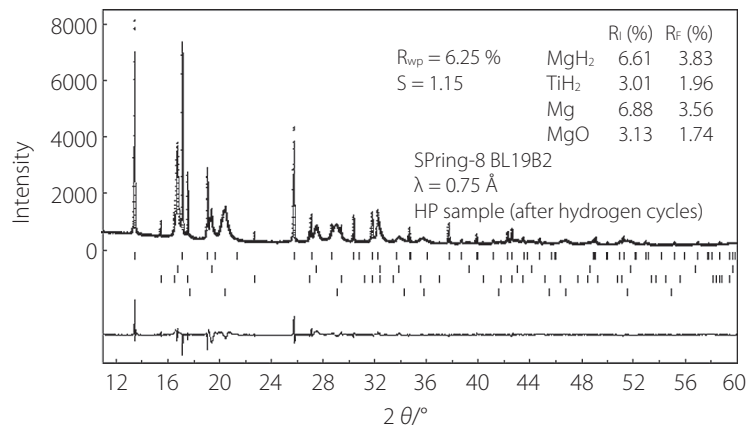

Figure 3: Synchrotron XRD pattern and the Rietveld refinement results of the HP Mg-Ti hydride sample after cycling (The phases are (from top to bottom) α-MgH$_2$, TiH$_2$, Mg and MgO.)
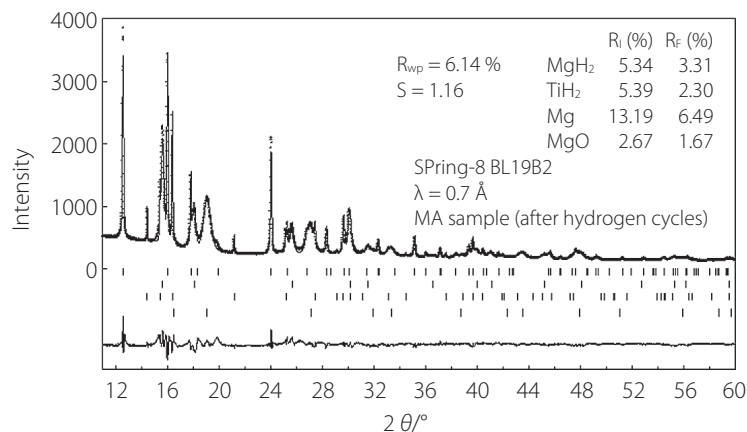

Figure 4: Synchrotron XRD pattern and the Rietveld refinement results of the MA Mg-Ti hydride sample after cycling (The phases are (from top to bottom) α-MgH$_2$, TiH$_2$, Mg and MgO.)
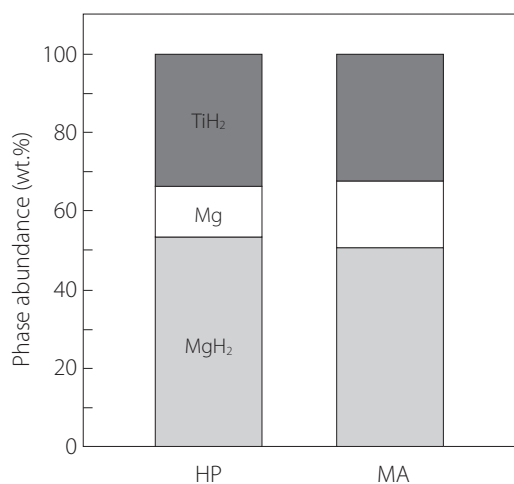
Figure 5: Phase abundance of the HP and MA Mg-Ti hydride samples after cycling obtained by the Rietveld refinement

ples obtained by the Rietveld analysis. Two samples prepared by different techniques form an equivalent composition during the hydrogen cycles. Moreover, their DSC results, such as releasing and restoring temperature and the peak areas, are very similar. These results suggest that the Mg-Ti-H samples exhibit an equivalent hydrogen storage mechanism.

The reversible hydrogen storage behaviors were also observed in the other HP Mg-M-H samples (M = Sc, V, Zr, Nb, Hf and Ta) (Kyoi et al., 2004b; Rönnebro et al., 2005; Sato et al., 2006; Kyoi et al., 2007; Kyoi et al., 2008a; 2008b; Takasaki et al., 2007a;b; 2013). The super-lattice type Mg_7MH_{16} phases (M = Ti, V, Zr, Nb and Ta) were decomposed during the hydrogen releasing. Simple fcc-lattices, such as Mg-Zr-H (Kyoi et al., 2008b; Takasaki et al., 2007b) and Mg-Sc-H (Takasaki et al., 2013), were maintained during the hydrogen releasing and restoring process. The ratio of the atomic radii between Mg and M would be one of the reasons for determining the M arrangement of the fcc phase. For the super-lattice-type one, the Mg/M for M = Ti, V, Nb and Ta are approximately 0.85-0.9, while for the simple fcc one, the Mg/M for M = Sc and Zr, are almost equivalent to 1. The Mg/Hf is 0.96, containing both the super-lattice and simple fcc phases. After the hydrogen cycles, a simple Mg-Hf-H phase remained (Kyoi et al., 2008b).

A series of HP samples exhibited an equivalent reversible hydrogen storage property, while the fcc lattice was decomposed. It is considered that an Mg-Ti-H solid solution, namely the partially Ti-substituted MgH_2 and/or Mg-substituted TiH_2, is maintained even after the Mg_7TiH_{16} decomposition and contributes to the reversible hydrogen storage capability. For example, the fcc Mg-Zr-H sample exhibits the equivalent hydrogen storage behaviors to the Mg-Ti-H sample (Takasaki et al., 2007b). The hydrogen strongly attached to the Zr would play the role of maintaining the Mg-Zr-H solid solution, while

the H bonded to the Mg would be reversibly released and restored (Takasaki et al., 2007b). For the Mg-Ti-H sample, the H attached to the Ti and Mg would contribute to maintaining the ternary composition and reversible hydrogen storage characteristics.

For Mg : Ti = 7 : 1 in the initial mixture, the XRD patterns of MgH_2 and TiH_2 were broadened during the MA treatment, but their original patterns were maintained. The lattice defects in MgH_2 and TiH_2 due to the MA treatment would be substituted by Ti and Mg, respectively, and the Mg-Ti-H solid solution, which exhibits the reversible hydrogen storage property equivalent to that of the HP sample, was formed. As previously reported, the MA sample of Mg:Ti = 1:1 mainly consists of Ti-rich fcc phases (Asano and Akiba, 2009; Asano et al., 2009). In this case, the hydrogen releasing temperature was higher than 773 K under 4.5 MPa H_2 pressure.

4. Summary

The high-pressure (HP) synthesized Mg_7TiH_{16} phase exhibited reversible hydrogen releasing and restoring around 600 K and 550 K, respectively. These behaviors bear a resemblance to the mechanically-alloyed (MA) $7MgH_2+TiH_2$ sample. After the hydrogen cycles, the fcc Mg_7TiH_{16} phase was decomposed. The phase abundance of the HP sample is almost equivalent to that of the MA one. These results indicate that both samples have an equivalent hydrogen storage mechanism, namely, the partial hydrogen atoms maintain the ternary Mg-Ti-H solid solution and the remaining hydrogen contributes to the reversible releasing and restoring characteristics.

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