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Reactivity Improvement of Magnesium with Hydrogen by Carbon Nano-Material Mixing

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Abstract

Proposing magnesium as a hydrogen storage material, we demonstrate quite interesting results of carbon nano-materials mixed into magnesium by mechanical milling in this study. Higher hydrogen reactivity can be obtained by multi wall carbon nano-tube (MWCNT) mixing which may enlarge the diffusion path in the sample powder particles. As a result, Mg with 0, 10, 20, 40 and 60 mass% of MWCNT exhibits drastically modified hydrogen absorption and desorption kinetics with more than 5 mass% H (including weight of catalyst) at 573-673K within 10min. under 6MPa of H_2.

1 Introduction

Hydrogen is expected in many application fields, especially in H_2 storage technique for fuel cell vehicle, where the available hydrogen density is an important factor. If the technological standard is considered, the hydrogen density of 5～7 mass% is required for the fuel cell vehicle [1]. Liquid hydrogen, which is one of the way of H_2 storage, realizes about 5 mass% of hydrogen density including the mass of container. However, the liquid hydrogen needs a lot of energy in cooling and yields unavoidable gas boil-off. On the other hand, H_2 storage materials exhibit higher hydrogen density even at room temperature. The volume density is, in most cases, higher than liquid hydrogen. However, a typical hydrogen storage material of $LaNi_5$ exhibits lower hydrogen density of only 1.4 mass%, which cannot be used for the vehicles.

Alkali-earth element of magnesium has been expected as a hydrogen storage material with a large hydrogen capacity. However, low hydrogen reactivity even at higher temperature is a significant problem for the practical utilization. Recently, for improving the sorption characteristics, we have reported the reaction kinetics of chemical hydrides with higher hydrogen density by mixing rare-earth oxide [2]. We have concluded that catalytic effect seems to be attributed to the hydrogen diffusion path generated in the hydride phase layer by rare-earth oxide.

In this study, carbon nano-material mixed into Mg has been demonstrated where the hydrogen sorption reactions and the density of hydrogen are drastically improved.

2 Experimental

2.1 Sample preparation

The mixture of MgH_2 (98%) and MWCNT(φ20~50nm) was mechanically milled in a rotary mill (IRIE SHOKAI Co., Ltd)(see Figure 1). MgH_2 and MWCNT were obtained from Wako Pure Chemicals. The mixing ratios of CNT / Mg were 1, 10, 20, 40 and 60 mass% in weight ratio, respectively. In this study sample preparation was carried out in a glove box under argon atmosphere. The condition of ball milling process is shown in Table 1.

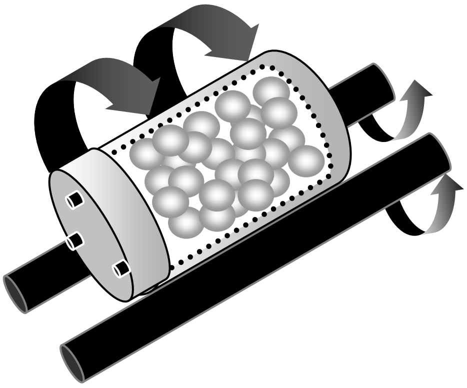

Figure 1: Rotaly ball-milling.

Table 1: Ball milling condition.

Rotating rate	180 rpm
Milling samples	Mg, MWCNT
Total weigth of the sample	1.5 g
Millimg period	25 hr
Milling atmosphere	Ar (99.999%)
Ball diameter and number	0.95mm×35
Volume ratio of vial vs. balls	1.7 : 1
Outside / Inside vial diameter	70.59 / 39.75 mm
Capacity of vial	70.33cm^3
Materials of vial / ball	18Cr-12Ni-2.5Mo-Low C. / 18Cr-8Ni

2.2 Sample analyses

The micro structure observation was carried out using SEM (Hitachi, S-3200N) and FE-SEM (Hitachi, S-4200) for the sample after ball milling. In addition samples were also observed by STEM (Hitachi HF-2200, 200kV) EDX (NORAN) and FIB (Hitachi) after the thinning preparation.

2.3 Measurement of hydrogen reactivity

Hydrogenation was carried out using high pressure Sievert's type apparatus. Sample in reaction tube was heated up to 673K . Dehydrogenation was carried out at 673K for several hours and cooled down to 573K under the high vacuum. After that, high purity hydrogen (7N) of 6MPa was then supplied at 573K. Afterwards hydrogenation was carried out at 573K. The process was repeated and initial reaction rate and hydrogen amount absorbed confirmed to be stabilized.

3 Results and Discussions

3.1 STEM image after ball milling

STEM image of MgH_2+ 40mass% MWCNT mixture after the ball milling of 25 hours is shown in Figure 2-(a). Fibrous form of WMCNT can be recognized. TEM image of MgH_2 + 40mass% MWCNT is shown in Figure 2-(b). Pillar form at the lower left is WMCNT. The difference of contrast indicate hole structures of MWCNT. From the figures we can understand that MWCNT is not broken even after long time of ball milling.

TEM cross section image and elementary distribution measured by EDX for the sample of Mg+ CNT 40mass% are shown Figure 3. Fiber forms of MWCNT can be confirmed also in the sample particle of Mg. Distribution of carbon indicates observed by EDX analysis, MWCNT exists also in the granulose Mg particle. These results show the possibility that MWCNT supply Mg particle diffusion passes for hydrogen inside.

3.2 Hydrogen Reactivity

Hydrogenation curves of MgH_2 and MgH_2 + MWCNT under 1MPa H_2 at 573K are shown in Figure 4. Addition of MWCNT exhibits an extremely accelerated reaction rate of hydrogen absorption. The sample absorbs H of 4wt% (excluding catalyst) within 10min.

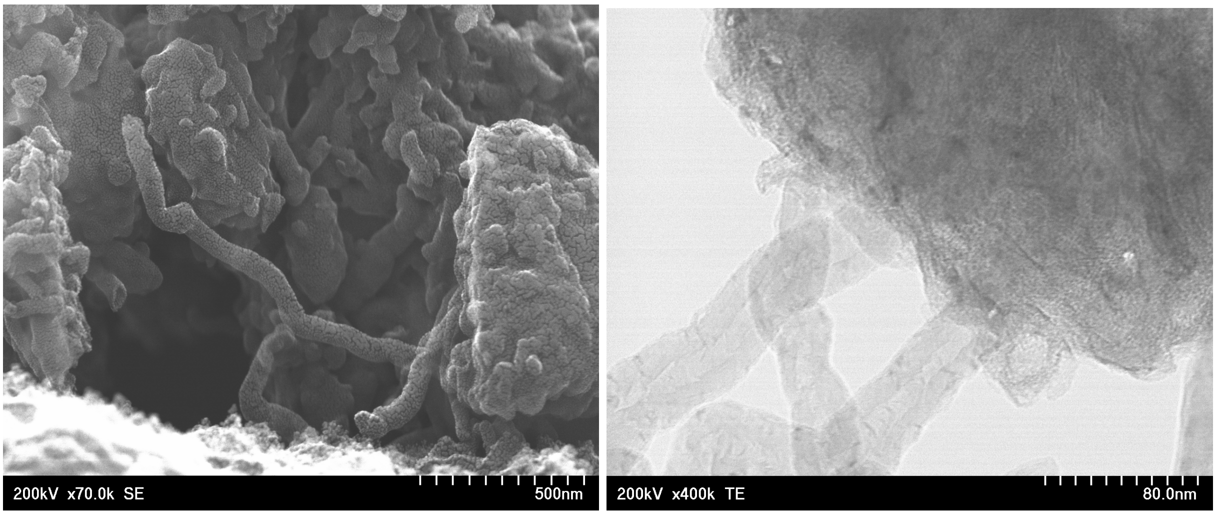

Figure 2: (a) STEM, (b) TEM images of After the ball milling of 25 hour of MgH_2+ CNT 40mass%.

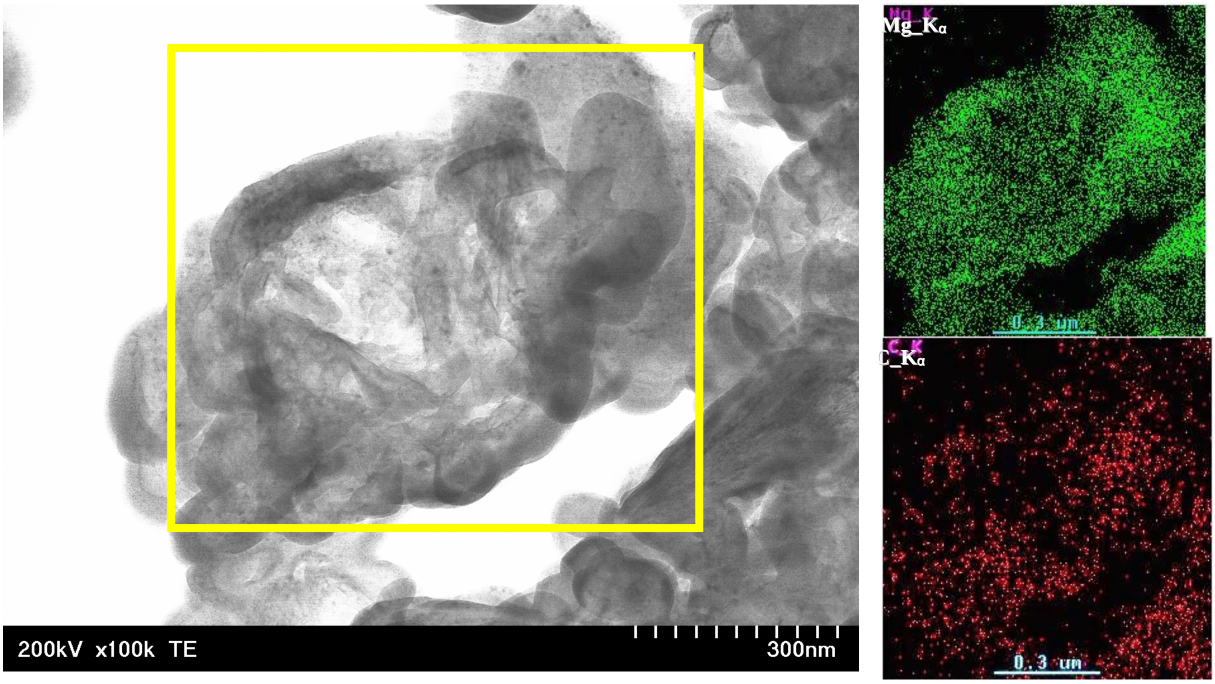

Figure 3: TEM and EDX images of Cross section observation of Mg+ CNT 40mass%.

In general, hydrogen absorption of Mg is controlled by diffusion of H atom through hydride layer in surface region. The precise reaction mechanism is not well known; however, catalysis of MWCNT distributed in the particle of Mg accelerates the diffusion of H atoms into the particle. Pressure dependence of the initial rate indicates a tendency of a change from diffusion to dissociation controlled reactions by the addition of MWCNT. The mechanisms of the reaction should be investigated further more.

Amount of MWCNT is also an interesting factor. Initial reaction rate and hydrogen absorption (including catalyst) at 10800 sec with different amount of MWCNT are shown in Figure 5. Initial reaction rate depends on the amount of MWCNT. From the Figure 5, increasing amount of MWCNT accelerates the initial sorption rate while decreasing the hydrogen density absorbed if the mass of MWCNT is included. In this study, therefore, 1~10mass% seems to be the best ratio of the mixture for both initial reaction rate and hydrogen absorption density.

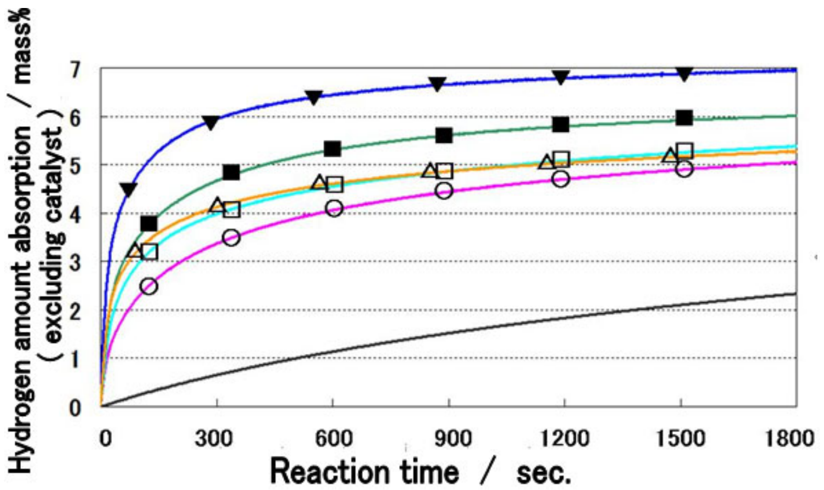

Figure 4: Hydrogen absorption of Mg and Mg + MWCNT with different amount of MWCNT.

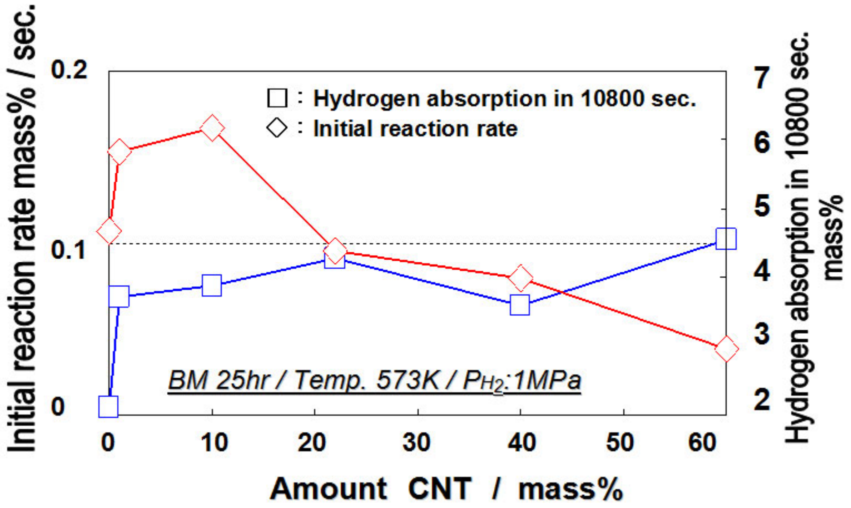

Figure 5: Initial reaction rate and hydrogen absorption density (excluding MWCNT) after 10800 sec for the sample with different amount of MWCNT.

4 Conclusion

A fuel cell vehicle needs to carry hydrogen of 7kg in the near future. In case of utilizing $LaNi_5$ (1.4wt% H), metal of 500kg is necessary. On the other hand, in case of Mg (6.0wt% H), only 120kg is enough for carrying the same amount of hydrogen, where the weight can be reduced to 25% if Mg is available.

Mg + MWCNT mixture by ball milling shows a more suitable reactivity for the practical hydrogen sorption reaction. Rate controlling step of hydrogenation of pure Mg is in generally considered as diffusion of H atom in magnesium hydride layer on the surface because of the ion bonding with matrix. In this study, mixing of MWCNT is demonstrated for realizing an increased reaction rate, where the MWCNT may give the paths of fast ab- and desorption. Additionally, amount CNT is a dominant factor for the sorption rate. By increasing amount

MWCNT, initial reaction rate also increases, while if the hydrogen density is considered, 1~10 mass% is the appropriate amount of the mixing.

References

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[2] Atsushi Uemura et al: J. Mat. Sci. Vol.72, No.3, p.224-228, 2008