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Mechanical alloying of graphite and magnesium powders, and their hydrogenation

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Abstract

Graphite and elemental magnesium (Mg) powders, whose chemical compositions were $C_{100-x}Mg_x$ ($0 \leq x \leq 40$ at.%), were mechanically alloyed (milled) in an argon gas atmosphere, and these powders were loaded with hydrogen in a high-pressure vessel at a temperature of 308 K. The initial hydrogen gas pressure for hydrogenation experiment was 4 MPa. The periodicity of the *c*-axis of the graphite crystal structure was destroyed completely for C_{100} powders and partly for the powder containing Mg at an early stage of mechanical alloying (MA), indicating the formation of a turbostratic structure (graphene) for all powders. Although elemental Mg still remained in Mg-rich powders ($C_{60}Mg_{40}$) even after longer MA (80 h), other powders reached to mostly the turbostratic structure with no sign of crystalline Mg. The maximum hydrogen concentration levels after hydrogenation for C_{100} powder were 0.1 wt.% after MA for 25 h and 0.4 wt.% after MA for 80 h, suggesting that nanostructured graphite uptakes more hydrogen. On the other hand, hydrogen concentration level for $C_{90}Mg_{10}$ powders was less than 0.1 wt.% after MA for 15 h, but it reached to about 1 wt.% after MA for 25 h, and dropped down slightly from 1 wt.% after MA for 80 h. Furthermore, hydrogen absorption occurred smoothly and quickly for $C_{90}Mg_{10}$ powders, although longer induction time was required for C_{100} powders. Further addition of Mg to graphite reduced the maximum hydrogen concentration level in the powders, and the powders containing more than 30 at.% Mg did not absorb hydrogen at all at 308 K.

Keywords: Mechanical alloying; Hydrogen storage; Graphite; Magnesium; X-ray diffraction

1. Introduction

After a report of hydrogen storage in single-walled carbon nanotubes by Dillon et al. [1], tremendous interest has been arisen for hydrogen storage in carbonaceous materials. Although hydrogen storage capacities of the carbonaceous materials at low temperature, which are dependent on specific surface area, those capacities reported seem to be reasonable. However, there seems to be controversy for the hydrogen storage capacities at around room temperature [2]. Beside hydrogen storage in advanced carbonaceous materials such as carbon nanotubes and graphite nanofibers, hydrogen storage in activated carbon and graphite has also drawn much attention.

Nanostructured graphite prepared by mechanical milling under hydrogen atmosphere (1 MPa) has been reported to absorb hydrogen (deuterium) up to 7.4 wt.%, in which hydrogen existed in two states; one in the graphite interlayers and the other as C–H bonding (dangling bond) [3]. Mechanical milling of magnesium (Mg) with graphite (approximately $C_{47}Mg_{53}$) in nitrogen atmosphere was reported to result in the generation of large amounts of dangling carbon bonds in the graphite, providing suitable sites for hydrogen atoms, in which at least two hydrogen states have been reported to exist; one in the form of C–H bonding in the nanostructured graphite and the other as a hydride in Mg [4].

After been motivated with those results, graphite and Mg mixtures were mechanically alloyed in the Mg concentration range between 0 and 40 at.% in this study. The phase variations after mechanical alloying (MA) and hydrogen storage capacities by gas phase hydrogen loading at a temperature of 308 K were investigated. The effect of addition of Mg to the graphite was also discussed.

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2. Experimental procedures

Commercially pure graphite and elemental Mg powders were used as starting materials in this study. The purity of both powders is 99.9%, and the mean grain diameter of graphite and Mg were 20 μm and 180 μm, respectively. The elemental mixtures with a chemical composition of $C_{100-x}Mg_x$ ($0 \leq x \leq 40$) were poured into stainless-steel vials (45 cm^3), which also contained stainless-steel balls. The ball-to-mixture weight ratio was approximately 8:1. The vials containing the elemental mixture and the balls were evacuated by a rotary-pump and then back-filled with an argon gas (99.99999%) several times in a glove box, and the final argon gas pressure was kept to be 0.1 MPa. MA was carried out by a Fritsch Pulverisette 7 planetary ball mill. The maximum ball acceleration was 15 g. To avoid any temperature increases during MA, the alloying period of 0.5 h was alternated with an equal rest time. Powder X-ray diffraction (XRD) measurements were made with Cu Kα radiation to identify the phases before and after MA for several times. The high-pressure hydrogenation was performed at a temperature of 308 K by using a high-pressure vessel made of stainless-steel. The initial hydrogen pressure was 4 MPa. Hydrogen concentrations in the powders were calculated from pressure change in the high-pressure vessel, which was monitored by a pressure transducer.

3. Results and discussion

Fig. 1 shows XRD patterns for the graphite (C_{100}) powders before and after MA for alloying times up to 80 h. The strong XRD peak from the (0 0 2) plane of the graphite (basal plane of hexagonal structure) observed before MA disappears completely at an early stage of MA (this peak cannot be visible even if one enlarges the scale of the vertical axis). The (1 0 0) and (1 0 1) peaks of the graphite which are thought to combine into a single peak between them (this is called the (1 0) diffraction peak, in which the third index is missing due to the structural breakdown), however, becomes lower in intensity but still remains even after MA for 80 h. These are due to weakly bonding forces (van der Waals forces) between carbon hexagonal layers while the strong covalent bonding (σ bonding) in the hexagonal layers, meaning that a basal cleavage occurs easily during MA. Two additional XRD peaks are also observed beside the (1 0) peak and at $2\theta \div 50^\circ$, particularly for the powder after MA for 10 h, that are unknown at this time. These XRD results clearly indicate that the graphite structure decomposes at an early stage of MA and turns to the turbostratic structure, in which carbon hexagonal layers still remain but the periodicity to the *c*-axis direction disappears because of missing of the (0 0 2) diffraction. Fig. 2 shows XRD patterns for $C_{80}Mg_{20}$ powders before and after MA for alloying times up to 80 h. The strong (0 0 2) peak becomes extremely weak and broad after MA for 10 h. This broad peak, however, still remains even after MA for 80 h, which is different from the result for the C_{100} powder. Although the degree of the turbostratic structure seems to be dependent on Mg concentration in the powders, the graphite in the $C_{80}Mg_{20}$ powders is also thought to turn to a turbostratic structure. Some XRD peaks for Mg remain until MA for 20 h, but disappear completely after additional MA for more than 40 h. The (1 0 0) and the (1 0 2) peaks turn easily into a broad combined single (1 0) peak after MA for more than 10 h. Further addition of Mg to the graphite powder made elemental Mg difficult to disappear (turn into amorphous state), but the graphite structure normally decomposed at an early stage of MA. The $C_{60}Mg_{40}$ powder, for instance, crystalline Mg still remained even after MA for 80 h, but the graphite structure was mostly decomposed into a turbostratic structure after MA for 10 h. Mean powder diameters of the graphite and Mg before MA were 20 and 180 μm, respectively, as mentioned earlier, but those for C_{100} and $C_{90}Mg_{10}$ powders after MA for 80 h were 1 μm and 9 μm, respectively, indicating MA reduced the mean powder diameters drastically.

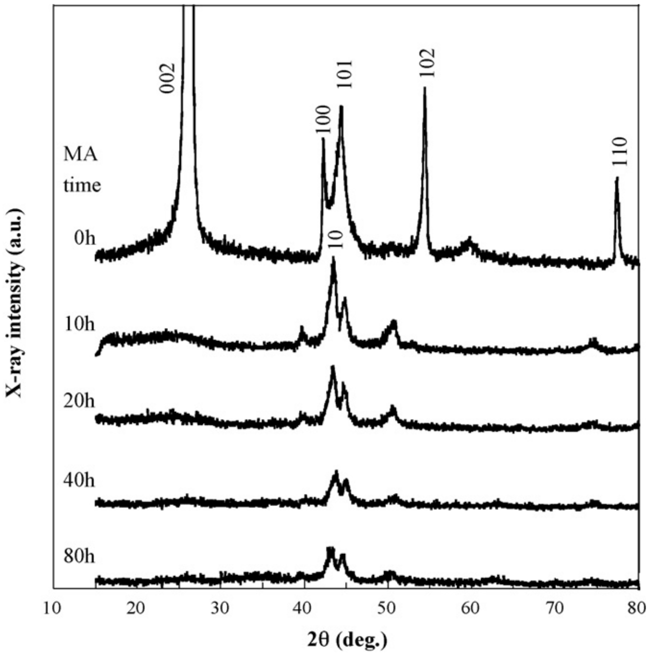

Fig. 1. X-ray diffraction patterns for graphite powders before and after mechanical alloying. The alloying time increases vertically downward from pattern to pattern.

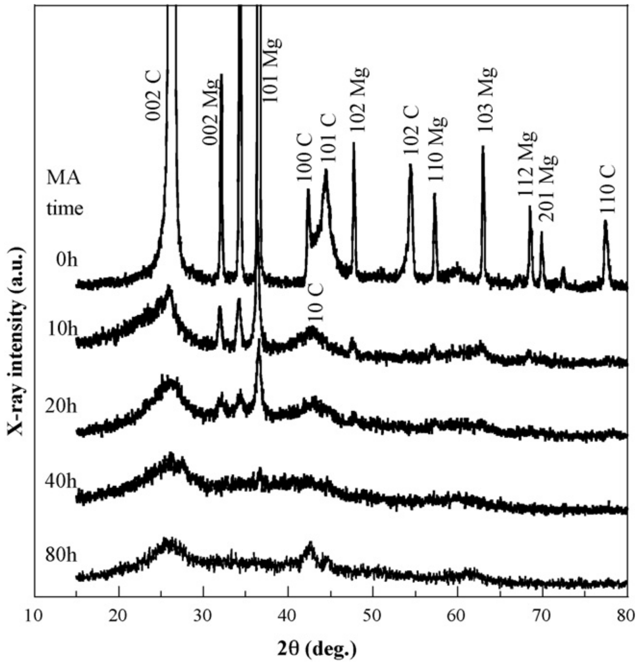

Fig. 2. X-ray diffraction patterns for graphite powders containing 20 at.% Mg before and after mechanical alloying. The C and Mg mentioned with indices mean ones for crystalline graphite and magnesium, respectively. The alloying time increases vertically downward from pattern to pattern.

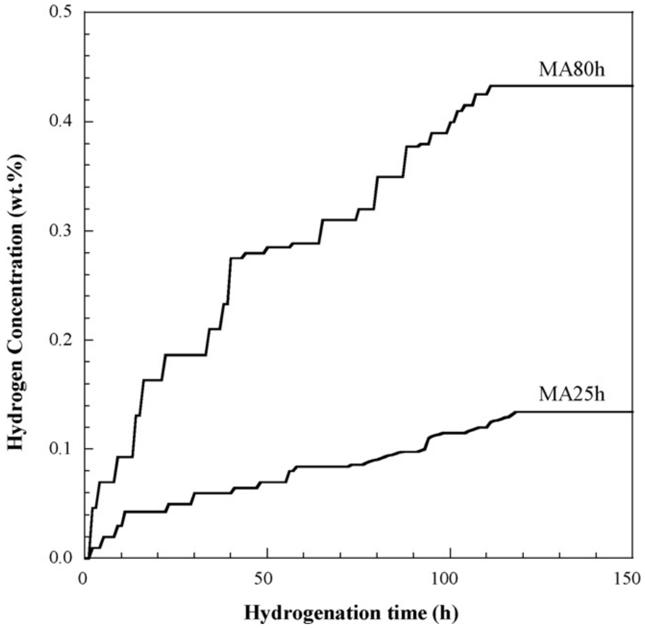

Fig. 3. Hydrogen concentration change during high-pressure hydrogen loading for graphite powders mechanically alloyed for 25 h and 80 h.

Hydrogen concentration change during high-pressure hydrogen loading for the C_{100} powders are shown in Fig. 3. Because the measurements were made at regular intervals in minutes, at the beginning, and in hours afterwards, hydrogen absorption plots seem not to be smooth. The maximum hydrogen concentration levels for C_{100} powders after MA for 25 and 80 h are about 0.1 wt.% and 0.4 wt.%, respectively, suggesting that nanostructured graphite uptakes more hydrogen. A long induction time (about 110 h) is needed to reach the maximum concentration levels for both powders. Fig. 4 shows hydrogen concentration change during high-pressure hydrogen loading for the $C_{90}Mg_{10}$ powders. The maximum hydrogen concentration level for $C_{90}Mg_{10}$ powders is less than 0.1 wt.% after MA for 15 h, but can be reached quickly, when compared with the results of C_{100} powders. The maximum hydrogen concentration level is raised to about 1 wt.% after MA for 25 h, with a fast absorption kinetics, but further alloying seems to reduce the maximum hydrogen level. It is implied that fine elemental Mg might stick on the nanostructured graphite powders during MA, acting as catalyst for hydrogen absorption, or that Mg atoms are intercalated between the carbon hexagonal layers, attracting hydrogen atoms inside the carbon hexagonal layers. Actually, the interlayer spacing of the graphite before MA was about 0.674 nm, but that of the graphene sheet obtained after MA for 10 h, particularly for $C_{90}Mg_{10}$ powders, was about 0.688 nm (about 2.1% increase), which also increased with increasing alloying time (about 10% increase after MA for 80 h). Some 3d transition metals such as Fe and Co were reported to show catalytic effect on hydrogen storage of nanostructured graphite in hydrogen atmosphere [5], and Ni [6] and alkali (Li and K) [7,8] were also reported to act as/like catalysts for amorphous activated carbon, and carbon nanotubes and graphite, respectively. The alkali-doping was reported to be very much affected by moistures [8]. Fig. 5 summarizes the maximum hydrogen concentratrion levels as a function of Mg concentration in the graphite powders. The numbers in the parentheses mentioned close to the data dots are MA time necessary to obtain a given hydrogen concentration level. The highest hydrogen capacity obtained in this study is about 1 wt.% for the $C_{90}Mg_{10}$ powders after MA for 25 h. Further addition of Mg to the graphite powders reduces the maximum hydrogen concentration level in the powders, and powders containing more than 30 wt.% Mg cannot absorb hydro-

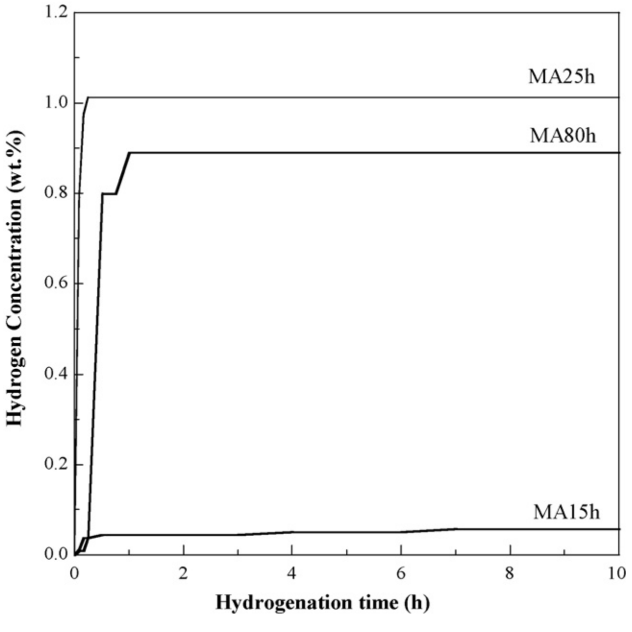

Fig. 4. Hydrogen concentration change during high-pressure hydrogen loading for graphite powders containing 10 at.% Mg mechanically alloyed for 15 h, 25 h and 80 h.

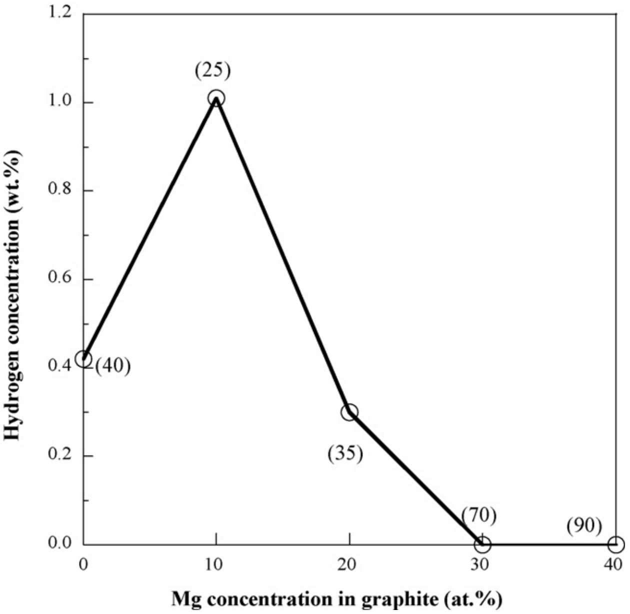

Fig. 5. The maximum hydrogen concentratrion levels as a function of Mg concentration in the graphite powders. Numbers in the parentheses mentioned close to the data dots show alloying time (h) necessary to obtain a given hydrogen concentration level.

gen at all at a temperature of 308 K. Recently, Jiang et al. have reported that Mg^+-implantation (∼5 at.%) to graphite provided efficient trapping centers and fast pathways for hydrogen diffusion [9]. Further works for optimizing Mg concentration level in the powders as well as alloying time are needed.

4. Conclusions

Powder mixtures of graphite and elemental magnesium (Mg) whose chemical compositions were $C_{100-x}Mg_x$ $(0 \leq x \leq 40)$ were mechanically alloyed in an argon atmosphere, and their mechanical alloying (MA) processes and the hydrogen storage capacities at a temperature of 308 K (the initial hydrogen pressure was 4 MPa) were investigated. The results obtained are summarized as follows:

1. The periodicity of the *c*-axis of the graphite structure was destroyed completely for C_{100} powders and partly for the graphite powders containing Mg at an early stage of MA. This indicates that a turbostratic structure (graphene), in which carbon hexagonal layers still remain without showing the periodicity of the *c*-axis direction, were formed, although the degree of the turbostratic structure seems to be dependent on Mg concentration in the powders.
2. Although crystalline Mg still remained even after longer MA for powder containing 40 wt.% Mg, the powder mixtures containing less Mg turned to mostly a turbostratic structure with no sign of presence of crystalline Mg after MA for 80 h.
3. The best hydrogen capacities were obtained from $C_{90}Mg_{10}$ powder in this study. Although the maximum hydrogen concentration level was less than 0.1 wt.% after MA for 15 h for $C_{90}Mg_{10}$ powder, it was raised to about 1 wt.% (with fast absorption kinetics) after MA for 25 h, but additional alloying reduced it slightly. Further addition of Mg decreased the maximum hydrogen concentration and the powders containing more than 30 at.% Mg did not absorb hydrogen at all.

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