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Effects of Mechanical Milling on Hydrogen Absorption Behavior of Carbon Micro Coils

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Effects of mechanical milling treatment on the hydrogen absorption of carbon micro coils (CMC) were investigated using a rising pressure technique (volumetric method) and a thermal desorption spectrometry (TDS). At a temperature lower than R.T., the milling treatment within 30 min for the as-grown CMC with an amorphous structure has brought about an increase up to 25 % (in maximum) of the hydrogen absorption. Moreover, by milling, the hydrogen absorbing ability of the crystallized CMC, with which the hydrogen hardly interacted, has been able to be recovered up to the absorption level of the as-grown CMC. Heavy milling for 1 h or more, however, resulted in the decrease of the absorbing capacity. In TDS measurements from R.T. to 1200℃ for the milled CMC heat-treated at 500℃ under 0.1 MPa hydrogen gas, another desorption peak of hydrogen was observed at about 600℃, in addition to the peak ranging from 850℃ to 900℃ caused by pre-existing hydrogen and also observed the remarkable increase of desorved hydrogen based on this new peak. This fact suggests that the milling has contributed to generate new absorbing sites of hydrogen. The addition of Ti powder to CMC on milling would lead to an increase of the sites.
Key words: hydrogen absorption, carbon micro coil, milling treatment, thermal desorption spectroscopy

1. INTRODUCTION

Up to date, many articles on hydrogen storage for many carbon-based materials have been reported,[1-11] because of the expectancy as one of the energy storage materials with light weight. With regard to the hydrogen storage capacity the reported values have been considerably scattered. Recently, there have been reports in which the hydrogen uptake is lower than 0.1 wt% for graphitic nanofibers (GNFs) under 11MPa at 27℃,[12] not to be appreciable above background for carbon nano-structured materials under 11MPa from -73 to 497℃[13] and less than 0.2 wt% under 4.5 MPa at room temperature.[14] In carbon micro coils (CMC) with an almost amorphous structure, we have obtained the high repeatability of hydrogen absorption, and the higher absorption ability (0.12 to 0.18 mass%) than those of other carbon materials at the lower temperature range than room temperature, although the specific surface area of the CMC is one tenth of that of the activated carbons. Moreover, it has been suggested that the disordered configuration of carbon atoms plays an important role as an absorbing site of hydrogen.[15]

In this paper, the effects of mechanical milling treatment on the hydrogen absorption behaviors of the CMC will be presented.

2. EXPERIMENTAL

2.1 Carbon micro coil (CMC) samples and mechanical milling treatment

The as-grown CMC, which has been prepared by a catalytic pyrolysis of acetylene at 750-800℃, [16-23] has an almost amorphous structure and contains about 1 mass% hydrogen. They have a 100 μm to 10 mm coil length, 1 to 5μm coil diameter, 0.1 to 0.5 μm coil pitch and about 100 m^2/g specific surface area.[24,25] The amorphous state is very stable and the apparent graphite layers are not observed. However, when the as-grown CMC was heat-treated at higher than 2500℃ for 3h, it has crystallized in just the state maintaining the morphology of coil. The graphite layer space (d) is 0.341 nm.[25]

The mechanical milling of CMC has been performed for 1 min to 16 h at room temperature (R.T.) using a planetary ball mill (P-7 type, Fritsch Co., Ltd., Germany). CMC samples of about 300mg were charged into a silicon-nitride rotatory pot with 45 ml together with zirconia beads with 5ϕmm (about 120 pieces) under 0.1 MPa Ar atmosphere. The revolution speed of disk and the rotation speed of pot were 800 and 1600 rpm, respectively, in every milling run. In some of milling runs, a very small amount of Ti powder, which had been fully degassed by heating to 850℃ under an ultra high vacuum condition for 30 min, was added.

2.2 Measurement of absorbed hydrogen

The hydrogen absorption for CMC was examined from the temperature of liquid nitrogen to R.T. under a high hydrogen pressure, using a volumetric type experimental apparatus as is shown in Fig. 1. About 200 mg of CMC sample was placed inside a high pressure chamber of 100 ml, and kept for 1 h in the chamber filled with 10 MPa of hydrogen at R.T.. Subsequently,

the chamber was cooled to the liquid nitrogen temperature. When the temperature of the chamber reached equilibrium, the pressure of hydrogen was reduced to 0.1 MPa and then the chamber was evacuated up to 10^{-3} Torr in 2 min. After the chamber was sealed and kept for 30 min in vacuum, it was removed from the liquid nitrogen vessel and then exposed to air. Using a capacitance manometer, the increase in pressure of the chamber due to desorbed hydrogen and rising temperature was measured as a function of time for more than 1000 min from the point that the chamber was sealed. The amount of desorbed hydrogen was calculated from the equilibrium pressure at R.T..

In order to investigate the hydrogen absorption ability at a higher temperature region than R.T., TDS (thermal desorption spectroscopy) measurements for about 1 mg sample were tried up to 1200℃ with the heating rate of 20℃/min under an ultra high vacuum condition. Here, the hydrogen charging to the sample has been attempted at 500℃ for 1 h under 0.1 MPa hydrogen stream, using a modified TG-DTA system.

SEM, TEM and XRD investigations into milled samples have been also tried side by side with the above experiments.

3. RESULTS AND DISCUSSIONS

3.1 Hydrogen absorption behaviors at lower temperature than R.T. (volumetric measurement)

Hydrogen absorption behaviors for the mechanically milled samples of as-grown CMC in various milling time is shown in Fig. 2. In mild milling for shorter than 30 min, the hydrogen absorption ability of milled samples has greater values than the as-grown CMC. The maximum value was obtained in 15 min milling and the pressure increase was about 25% of that of as-grown CMC. While, the hydrogen absorption ability has decreased by heavy milling for long time though tending to increase gradually with milling time. Figure 3 shows X-ray diffraction patterns of these milled samples. The as-grown CMC has an almost amorphous structure, although it is ordered in short range. Milling treatment lead the as-grown CMC not only to fine, but also to promote the amorphousness. In mild milling, coil-shaped fragments of CMC are still observed in the sample milled for less than 5 min, and by milling for 15 min they turned to many broken pieces with their diameter of less than 1μm. However, in the milling for a long time, the powder produced by milling has shown gatherings, as is shown in Fig. 4. The specific surface area of milled CMC become greater with the progression of milling. The present results suggest that the hydrogen absorption ability of milled CMC is not dependent on the specific surface area.

Hydrogen absorption ability of the as-grown CMC with amorphous structure decreases with the progress of crystallization by heat-treating at a temperature higher

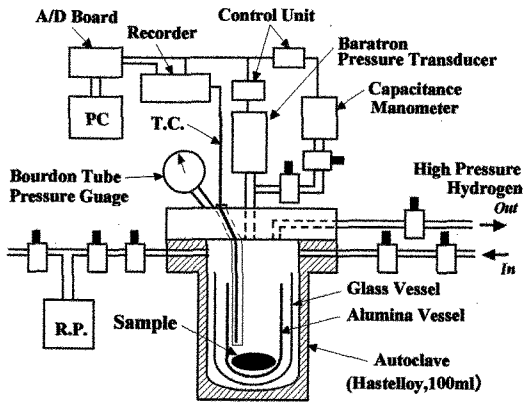


Fig. 1 A scheme of volumetric type measuring apparatus of hydrogen absorption at low temperature under high hydrogen pressure. T.C.: thermo coupling, R.P.: rotary pump.

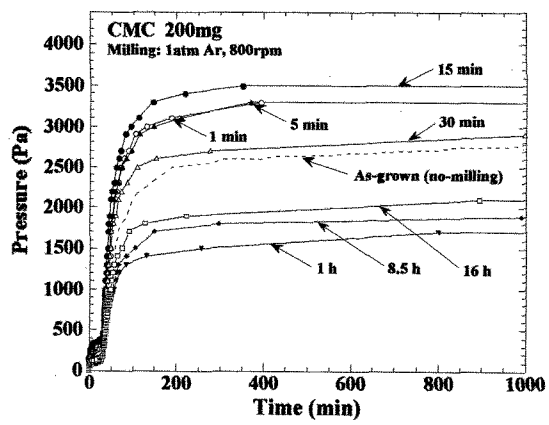


Fig. 2 Hydrogen absorption behaviors for CMC samples mechanically milled for various milling time.

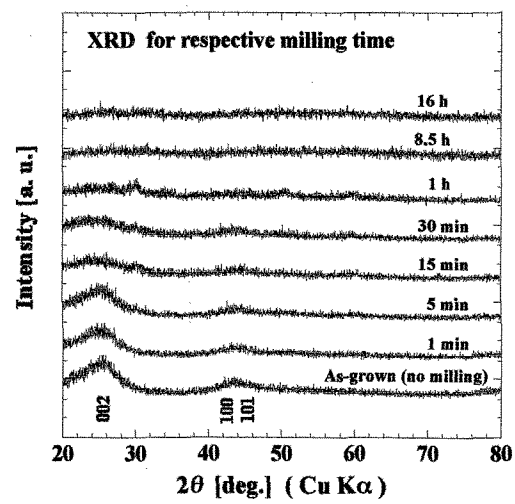


Fig. 3 X-ray diffraction patterns of mechanically milled CMC samples.

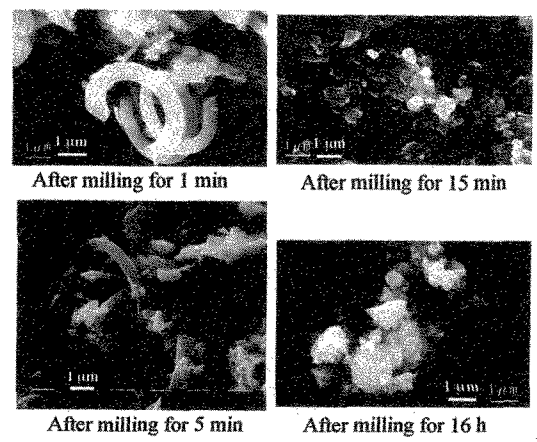


Fig. 4 SEM images of mechanically milled CMC samples.

than 1100℃, and by heat-treating at higher than 2500℃ it almost crystallizes. [15] The crystallized CMC did not absorb the hydrogen at all. By mechanical milling the crystallized CMC only for 15 min, however, the hydrogen absorption ability has been remarkably recovered up to the absorption level of the as-grown CMC, as shown in Fig. 5, although it has become the half level in the milling for long time (1h).

High resolution TEM images of CMC crystallized at 2500℃ and its mechanically milled CMC samples for 15 min are shown in Fig. 6. In this figure, it is observed that the c-layers of crystallized CMC are cracked and disorded by milling for 15 min. Such a disordered lattice configuration seems to contribute the increase of hydrogen absorption ability.

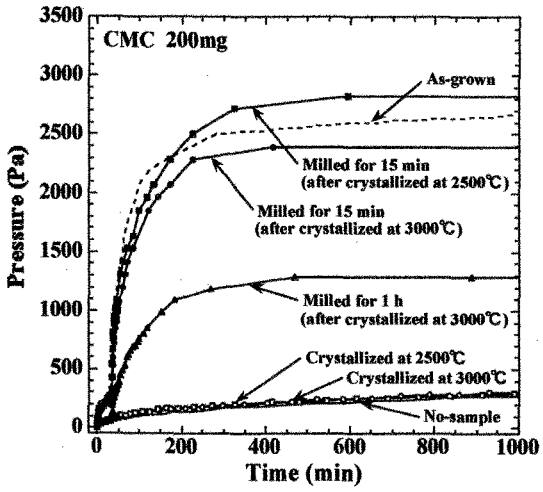
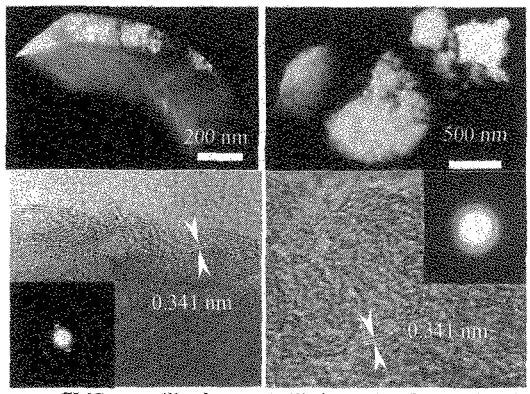


Fig. 5 Hydrogen absorption behaviors for crystallized CMC by heat-treating at a high temperature and its mechanically milled CMC samples for 15 min and 1 h.



CMC crystallized at 2500℃ for 3 h — Milled sample of crystallized CMC for 15 min

Fig. 6 High resolution TEM images of CMC crystallized at 2500℃ and its mechanically milled CMC samples for 15 min.

3.2 Hydrogen absorption behaviors at higher temperature than R.T. (TDS measurement)

Figure 7 shows the TDS spectra of hydrogen desorbed from as-grown CMC and two kinds of mechanically milled CMC samples, 15 min and 1 h. Here, the heating rate is 20℃/min. A large desorption peak of hydrogen is observed at the temperature range from 800℃ to 900℃ in the spectrum of as-grown CMC. This peak is caused by the dissolution of acetylene including the CMC. From the area of this peak, the hydrogen content is estimated as more than 0.5 wt%. In milled samples, the peaks become broad and the building-up temperature shifts to a lower temperature side. Moreover, a shoulder-like peak at about 650℃ appears and this peak is more clear in the spectrum of the sample milled for 1 h. This suggests that a new hydrogen existing site in CMC has been produced by the milling treatment.

TDS spectrum of hydrogen desorbed from the hydrogen charged sample after milling of as-grown CMC for 1 h is shown in Fig. 8 in comparison with ones of the as-milled sample and the as-grown CMC. In the hydrogen charged sample, the hydrogen desorption has started to build up at 450℃ and the desorption rate has soon reached to a high level at 550℃. The hydrogen content is estimated as more than 1.5 wt%. It is clear that new hydrogen sites in CMC produced by the milling treatment acts additionally and effectively as hydrogen absorption sites.

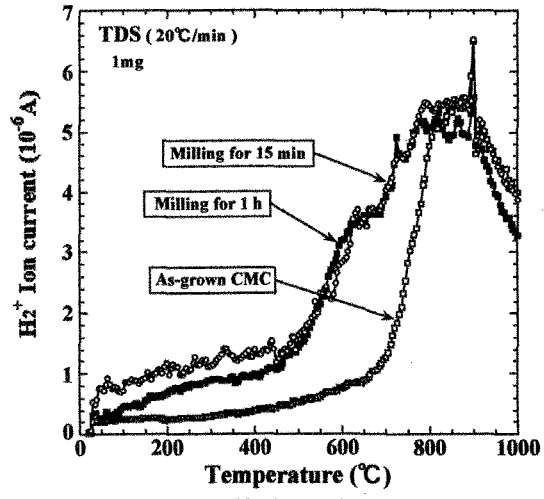


Fig. 7 TDS spectra of hydrogen desorbed from as-grown CMC and its mechanically milled CMC samples for 15 min and 1 h. Heating rate is 20℃/min.

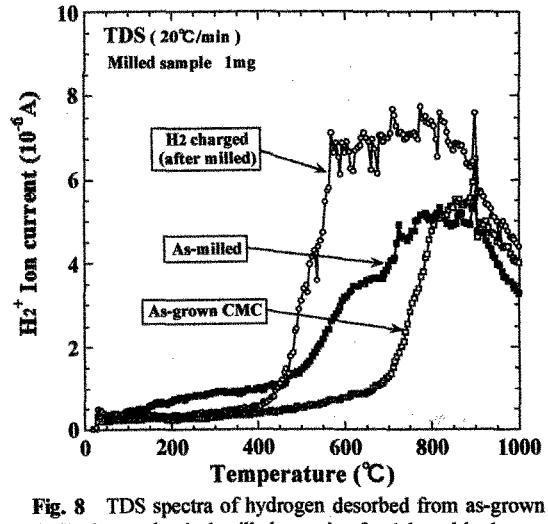


Fig. 8 TDS spectra of hydrogen desorbed from as-grown CMC, its mechanical milled samples for 1 h and hydrogen charged sample after milling for 1 h. Heating rate is 20℃ /min.

3.3 Effects of additional Ti on hydrogen absorption behavior

Hydrogen absorption ability of as-grown CMC has decreased by milling treatment for 1 h in spite of increasing its specific surface area. But, adding a very small amount of Ti powder on milling makes the ability better, as is shown in Fig. 9. Only Ti powder has not interacted with hydrogen in the lower temperature region than R.T., as is shown in this figure. These facts suggest that the existing of Ti in milled CMC contributes not to the increase of specific surface area but to the yielding of the absorption sites.

TDS spectra of hydrogen desorbed from two kinds of CMC samples, as-milled samples and hydrogen charged ones after milling, which were milled together with a very small amount of Ti powder for 1 h, are shown in Fig. 10. By adding Ti powder, the amount of desorbed hydrogen has increased and the temperature of main desorption peak is shifted to a lower temperature side. While, the shoulder-like peak at about 650℃ which has been observed in the milled sample of as-grown CMC, as shown in Fig. 7, becomes not to be conspicuous with the content of Ti.

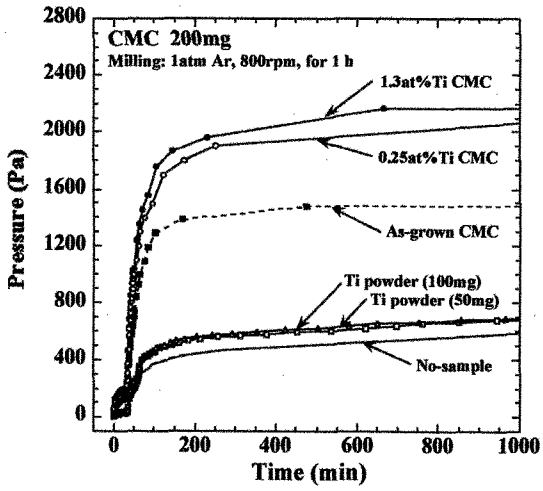


Fig. 9 Hydrogen absorption behaviors in lower than R.T. for two kinds of samples milled for 1h: as-grown CMC and ones added a very small amount of Ti powder on milling.

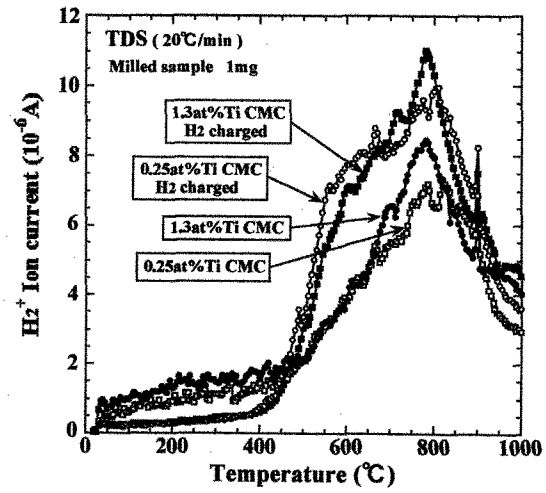


Fig. 10 TDS spectra of hydrogen desorbed from two kinds of CMC samples milled together with a very small amount of Ti powder for 1 h. One is as-milled samples and another hydrogen charged ones after milling. Heating rate is 20℃/min.

4. CONCLUSIONS

Concluding remarks are as follows.

In volumetric measurement at the lower temperature than R.T., a short-time mechanical milling for only less than 30 min is effective to increase the absorption ability either in the as-grown CMC or, especially, in the crystallized CMC, no interacting with hydrogen at all.

In TDS measurement at the higher temperature than the R.T., by mechanical milling treatment of as-grown CMC, the desorption peaks of pre-existing hydrogen become more broad and the building-up temperature of desorption shifts to a lower temperature side. Moreover, a shoulder-like peak at about 650℃ appears and this hydrogen existing sites in CMC have acted effectively in hydrogen absorption of CMC. That is, the milling treatment of as-grown CMC is able to bring the hydrogen absorption ability in higher than R.T..

By adding a very small amount of Ti powder on milling, the hydrogen absorption ability of CMC has been improved in both temperature ranges, lower and higher than R.T.. Existing of Ti in milled CMC sample tends to let down the both temperatures, built-up and peaked, of the hydrogen desorption in TDS.

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