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Hydrogen Absorption of Carbon Micro Coils

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Hydrogen absorbing behavior for micrometer scale carbon coils with a double-helical structure (CMC) was investigated using a rising pressure technique (volumetric method) and a thermal desorption spectrometry (TDS). At a temperature lower than R.T., the remarkable hydrogen absorption was observed in the as-grown CMC with an amorphous structure. The maximum values of pressure caused by the desorbed hydrogen were three to four times greater than those of activated carbons. Moreover, the pressure indicated an increase up to 20 % in maximum by pre-heating the as-grown CMC from 700℃ to 1000℃. The capacity of absorbing hydrogen was 0.12 to 0.18 mass%, exhibiting a high repeatability. It, however, decreased with the development of crystallization, and hydrogen hardly interacted with the CMC crystallized by pre-heating at a temperature higher than 2500℃. At the temperature range from R.T. to 500℃ under 0.1 MPa hydrogen gas, no hydrogen interacted with both types of CMC, i.e., as-grown and crystallized.

Key words: hydrogen absorption, carbon micro coil, thermal treatment

1. INTRODUCTION

Carbon materials have been expected as light weight energy storage materials in the future. Recently, many researchers have reported on hydrogen storage by carbon-based materials such as activated carbon (AC),[1-4] graphite intercalation compounds (GIC),[5,6] and carbon nanotubes (CNTs).[7-10] The hydrogen storage capacity was found to be 11.26 mass% for tubular graphite nanofibers (GNFs), 67.55 mass% for herringbone GNFs, 53.68 mass% for platelet GNFs, and 4.52 mass% for graphite, under the application of 11.35 MPa hydrogen pressure at 25℃ for 24 h.[11] These extraordinary high values caused avalanche of research on carbon nano-tubes and fibers. However, nobody has been able to reproduce these results up to now. In contrast with the above values, there have been reports in which the hydrogen uptake is lower than 0.1 wt% for 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 the room temperature.[14]

We have obtained a high repeatability of hydrogen absorption in carbon coils, and the higher absorption ability of hydrogen than those of other carbon materials in our experiment at the low temperature of -190 ℃ to room temperature, although the specific surface area of the carbon coils is one tenth of that of the activated carbons. The ability was, however, decreased with the development of crystallization in carbon coils.

In this paper, these results will be presented.

2. EXPERIMENTAL

2.1 Carbon micro coil (CMC) samples

Figure 1 shows an example of representative carbon coils prepared by a catalytic pyrolysis of acetylene at 750-800℃.[15-22] The as-grown carbon coils have an almost amorphous structure and contain about 1 mass% hydrogen. They have a 100 μm to 10 mm coil length, 1-5μm coil diameter, 0.1-0.5 μm coil pitch and about 100 m^2/g specific surface area.[23,24] So, they have been called carbon micro coil (CMC).

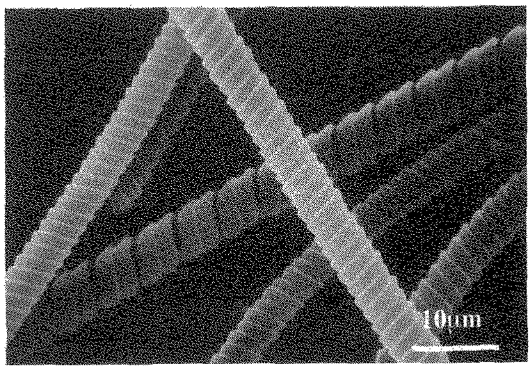

Fig. 1 SEM image of carbon coils which were prepared by the catalytic pyrolysis of acetylene at 750-800℃.

The amorphous state of the as-grown CMC is very stable and the apparent graphite layers are not observed even after heat treatment at 2000-2500℃ for 1 h in an Ar atmosphere.[20] However, when the as-grown CMC was heat-treated at 3000℃ for 6 h, their crystallization occurred with maintaining the morphology of the coils, as is shown in Fig. 2 (a) and (b).[24] Graphite layers were then developed by heat treatment with an inclination of 10-40° versus the fiber axis to form a "herringbone" structure with a specific surface area of ca. 8 m^2/g. The layer space (d) was determined to be 0.341 nm, which is slightly greater than the calculated value of d=0.336 nm (JCPDS, No.23-64). By ultrasonic wave irradiation during the growth of CMC, the c plane has tended to be more developed than that of the as-grown CMC, as is shown in Fig. 3.[25,26]

2.2 Measurement of absorbed hydrogen

The hydrogen absorption for CMC was examined from the temperature of liquid nitrogen to room one (R.T.) by loading a high hydrogen pressure, using a volumetric type apparatus as shown in Fig. 4.

A sample of about 200 mg of CMC was placed inside a high pressure chamber with a volume capacity of 100 ml, and kept for 1 h at R.T. in the chamber filled with 10 MPa of hydrogen. Subsequently, the chamber was cooled to the liquid nitrogen temperature. When the temperature within 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 the desorbed hydrogen and the rising temperature was measured as a function of time for more than 1000 min from the sealed point. The amount of desorbed hydrogen was calculated from the equilibrium pressure at R.T..

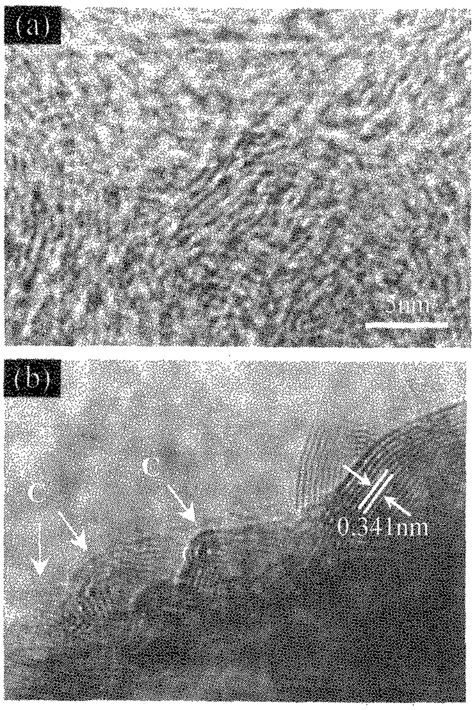

Fig. 2 High resolution TEM images of carbon coil. (a) as-grown CMC and (b) heat treated CMC at 3000℃ for 6 h. Symbol C shows capsule-like graphite layer.

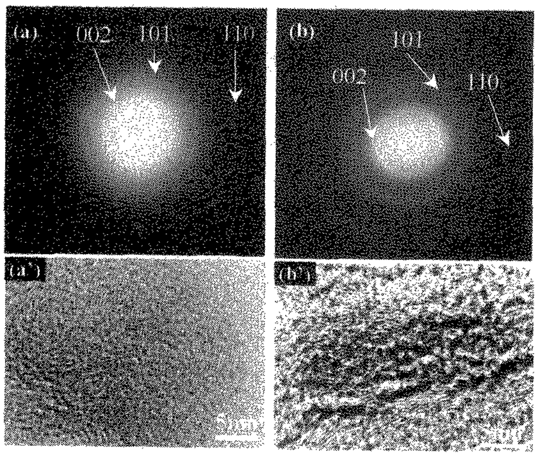

Fig. 3 High resolution TEM images and electron diffraction patterns. (a, a') as-grown CMC, (b, b') CMC grown under ultrasonic irradiation.

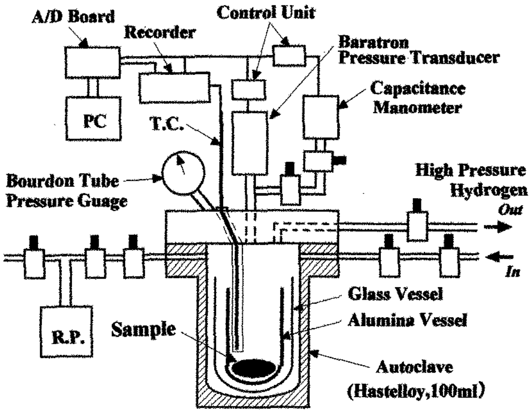

Fig. 4 A scheme of volumetric type measuring apparatus of hydrogen absorption at low temperature under high hydrogen pressure. T.C.: thermo coupling, R.P.: rotary pump.

In order to compare the hydrogen absorption ability of CMC with those of three types of activated carbons, i.e., coconut husk, coal carbon and woody carbon, were evaluated as hydrogen absorbers. Furthermore, they were heat treated at the respective temperatures from 700℃ to 3000℃ to clarify an effect of the crystal structure of CMC on the hydrogen absorption behavior.

Some TDS (thermal desorption spectroscopy) measurements were tried, additionally, to investigate the hydrogen absorption ability at the temperature range higher than R.T..

3. RESULTS AND DISCUSSION

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

The repetition of hydrogen absorbing ability for the as-grown CMC was firstly examined using the same sample. The results are shown in Fig. 5. Comparing the first run with the other runs, the hydrogen absorption behavior indicates a considerably good responsibility.

Figure 6 shows the hydrogen absorption property of the as-grown CMC with various coil length and other carbon materials, i.e., three types of activated carbon powders and graphite. It can be seen that the hydrogen absorption level of the as-grown CMC is superior to other carbon materials. And, the CMC with shorter coil length indicates a higher absorption level and the CMC grown under ultrasonic irradiation dose the highest.

From the increase of the chamber pressure due to desorbed hydrogen, it has been found that the as-grown CMC could absorb 0.12~0.18 mass% of hydrogen. This

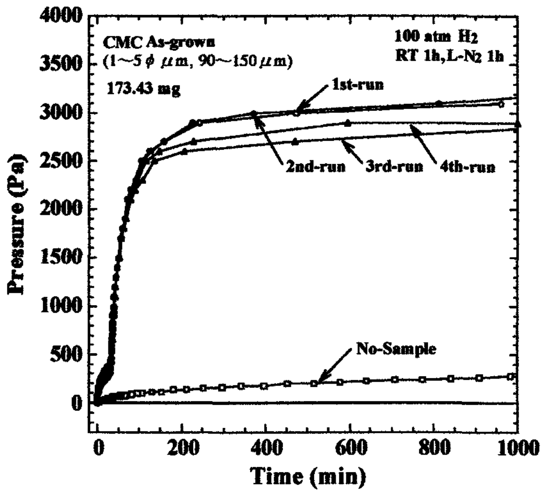

Fig. 5 Repeatability of hydrogen absorption for as-grown CMC under 10 MPa hydrogen at -190℃ to R.T..

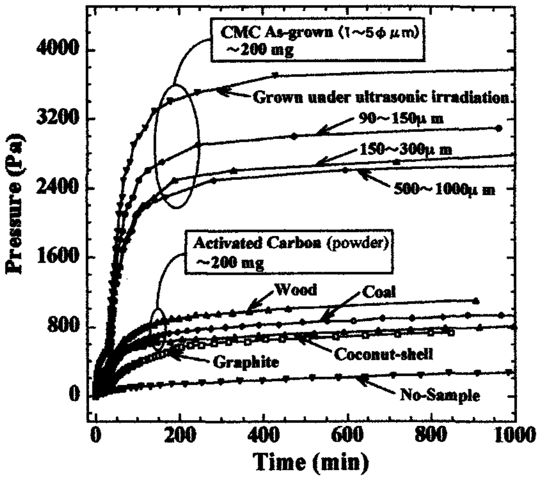

Fig. 6 Hydrogen absorption behaviors of as-grown CMC with various coil length, as-grown CMC under ultrasonic irradiation and other carbon materials, three types of activated carbon and graphite.

value is three to four times greater than those for commercial activated carbons, in the present experiment.

The specific surface areas of the as-grown CMC and AC are 90 m^2/g and 1000 m^2/g, respectively. Materials with a high specific surface area generally have an active property for the chemical and physical adsorption. Therefore, the higher hydrogen absorption of as-grown CMC will suggest that the hydrogen absorbing ability dose not depend on the specific surface area, but on nano-space structures existing in it.

The ultrasonic irradiated CMC allows higher hydrogen absorption level than those of other as-grown CMC, as shown in Fig. 6. In the structural features of the as-grown CMC and the ultrasonic irradiated one, as shown in Fig. 3, the 002 ring of the CMC grown under ultrasonic irradiation have an arc-like ring denoting a slight orientation of the c plane. This will suggest that the lattice vibration due to ultrasonic irradiation induces a structural disorder in the atomic arrangement leading to the increase in the hydrogen absorption.

Figure 7 shows the pre-heat treating effect of the as-grown CMC from 700℃ to 3000℃ on the hydrogen absorption behavior. The increments in hydrogen pressure for the CMC sample heat-treated at lower than 1000℃ indicate a temporary increase (up to 20%) of the absorption site of hydrogen which is caused the removal of the acetylene deposited on or included into the growing CMC.[27] In the mean time, the absorption level of hydrogen tends to decrease by heating from 1100℃ to 3000℃. X-ray diffraction patterns of the heat-treated CMC are shown in Fig. 8. The crystallization of the as-grown CMC gradually progresses by heating at a temperatures from 1100℃ to 2000℃, while the heating at higher than 2500℃ produces a high crystallization of the as-grown CMC. The high resolution TEM image of crystallized CMC shows the capsule-like c plane, as shown in Fig.2 (b), which will prevent the hydrogen adsorption and infiltration into CMC.

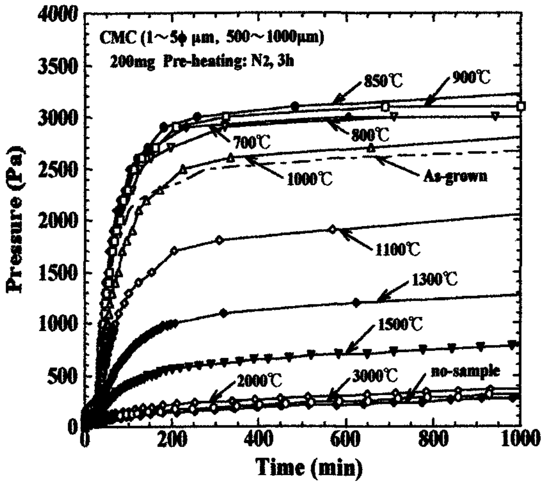

Fig. 7 Hydrogen absorption behaviors of CMC after heat-treating at respective temperature.

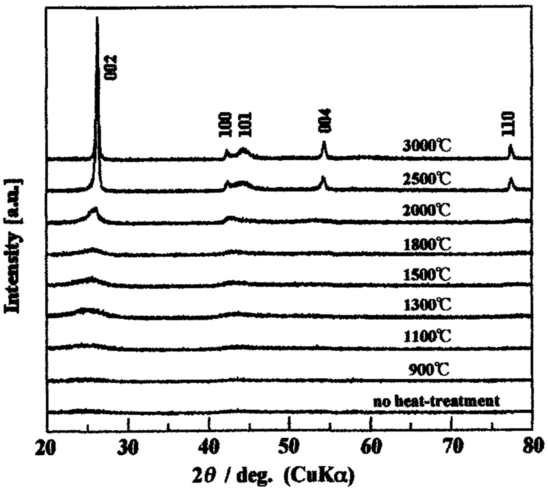

Fig. 8 X-ray diffraction patterns of CMC heat-treated at respective temperature.

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

Figure 9 shows TDS spectra of hydrogen obtained from the as-grown CMC and the hydrogen charged CMC after crystallized at 3000℃. Here, the hydrogen charging treatment has been attempted from 300℃ to

500℃ for up to 3h under 0.1 MPa hydrogen stream, using a modified TG-DTA system. The as-grown CMC was desorbed the pre-existing hydrogen of more than 0.5 wt% at the higher temperature region than 700℃. However, the crystallized one was almost never desorbed in spite of the hydrogen charging treatment.

Such a tendency of hydrogen absorption was also observed in the as-grown CMC, as is shown in Fig.10. In this figure, however, a small amount of desorbed hydrogen was recognized in the 3rd-run for the re-charged sample, after the pre-existing hydrogen had been desorbed. This hydrogen absorption ability will be brought by the disordered configuration of carbon atoms due to the dissolution of acetylene and the desorption of hydrogen, which is pre-existing hydrogen, in the 1st-run.

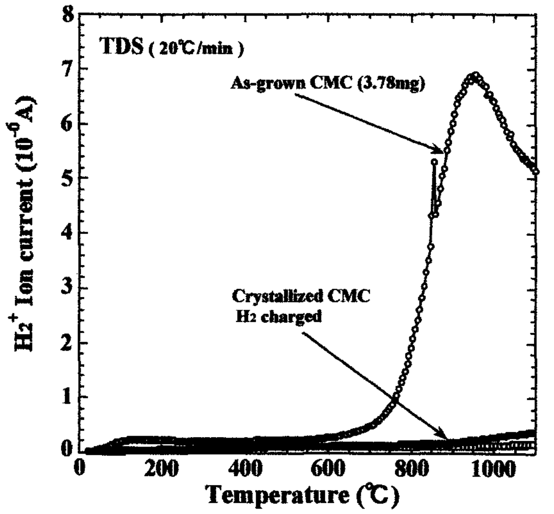

Fig. 9 TDS spectra of hydrogen for as-grown CMC and hydrogen charged CMC after crystallized at 3000℃.

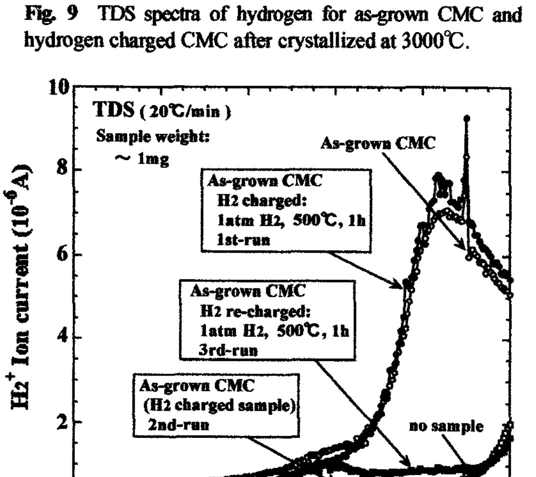

Fig. 10 TDS spectrum of hydrogen for hydrogen charging and no-charging as-grown CMC in subsequent runs.

4. CONCLUSIONS

Hydrogen absorption behaviors of CMC have been investigated at the temperature range from the liquid nitrogen temperature to R.T. under high hydrogen pressure. As-grown CMC with almost amorphous structure absorbs the hydrogen three or four times as much as other carbon materials. Its absorbing capacity of hydrogen is 0.12~0.18 mass% and behaves with a high repeatability in cyclic runs.

The hydrogen absorbing ability of CMC decreases according to the crystallization and the CMC heat-treated from 2500℃ to 3000℃ has not interacted with the hydrogen. On the other hand, by heat-treating from 700℃ to 1000℃, the hydrogen absorbing ability of the as-grown CMC increases up to 20 % in maximum value. These facts suggest that the heat treatment allows the carbon coils to control the absorption level of hydrogen.

At the higher temperature range than R.T., the CMC has almost no interaction with hydrogen.

The absorbing sites of hydrogen in CMC will be the disordered configurations of carbon atoms being yielded by the amorphous structure and by the removal and the decomposition of acetylene on and under the surface of the as-grown CMC.

Acknowledgment

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