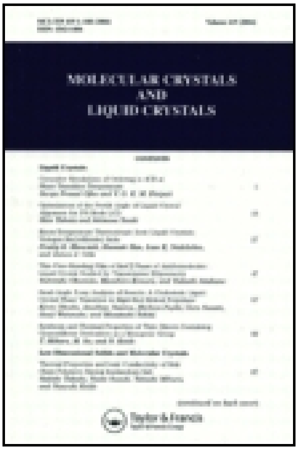

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Nanostructured graphite-hydrogen systems prepared by mechanical milling method

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NANOSTRUCTURED GRAPHITE-HYDROGEN SYSTEMS PREPARED BY MECHANICAL MILLING METHOD

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Nanostructured graphite was prepared by mechanical milling under a hydrogen atmosphere. Several samples obtained after different milling times were systematically examined to get fundamental information about the structures, hydrogen concentrations, and also hydrogen desorption properties. The hydrogen concentration reaches up to 7.4 mass% ($CH_{0.95}$) after milling for 80 h, and two desorption peaks of hydrogen molecule (mass-number = 2),

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starting at about 600 K and 950 K respectively, are observed in thermal desorption mass-spectroscopy in the sample. Below the temperature of the second desorption peak, at which recrystallization related desorption occurs, the nanostructured graphite is expected to retain its specific defective structures mainly with carbon dangling bonds as suitable trapping sites for hydrogen storage.

Keywords: nanostructured graphite; hydrogen storage; mechanical milling; defective structures; recrystallization

INTRODUCTION

Motivated by the first report by Dillon *et al.* [1], much attention has recently been directed towards the use of single-(multi-)walled carbon nanotubes for hydrogen storage [2–10]. Some of the reports on relationships between structures of the nanotubes and hydrogen storage abilities focus mainly on capillary effects of (bundles of) nanotubes. A capillary effect is achieved by firstly "opening the nanotube cap" by *pre-treatments* such as chemical etching, partial oxidation, and/or supersonic wave methods, and secondly trying to put hydrogen molecules into the capillary. The *pre-treatments* prior to hydrogenation, however, seem not only to open the cap but also to increase the number of defects like carbon dangling bonds, even in side-walls of the carbon nanotubes [11]. (Besides the nanotubes, graphite nanofibers [12–16], i.e., stacking of small platelet graphite, have a large number of defects at the geometrical edge area of platelets). Therefore, hydrogen storage abilities that are enhanced by the defective structures should be taken into account in carbon-related materials.

In the present work [17–19], nanostructured graphite was prepared by mechanical milling under hydrogen atmosphere. Different milling times were chosen and the samples were examined in order to get fundamental information about the structures and hydrogen concentrations, and also hydrogen desorption properties.

EXPERIMENTAL

300 mg of high-purity graphite powder (99.997% purity, ~200 μm) as a host sample and 20 steel balls of 7 mm in diameter were placed in a steel vial of 30 cc volume. The vial was equipped with a connection valve for evacuation and introduction of hydrogen. This was used to directly degas the host sample for 12 h below 1×10^{-4} Pa by a turbo-molecular pump. High-purity hydrogen or deuterium of 1.0 MPa was then introduced as an initial pressure. The host sample was mechanically milled using the planetary ball mill

apparatus (Fritsch P7) with 400 rpm for periods from 1 h to 80 h at room temperature. Before and after milling, all samples were handled in the glove-box filled with purified argon, so as to minimize oxidation and water-adsorption.

The samples thus prepared were systematically examined by X-ray and neutron diffraction (scattering) measurements, oxygen-combustion hydrogen analysis, oxygen analysis, BET adsorption examination with nitrogen gas, Raman spectroscopy with 532 nm-Laser of back scattering geometry, thermal desorption *mass*-spectroscopy, and thermogravimetry and differential thermal analysis. The apparatus for the *mass*-spectroscopy was especially designed and build for use inside the glove-box, permitting simultaneous measurements of TG and DTA without exposing the samples to air. Heating rate for the thermal analyses was 5 ~ 20 K/min. Fe-contamination after milling was estimated to be ~3 at.%.

RESULTS AND DISCUSSION

The combined analysis of X-ray diffraction and Raman scattering indicates that the milling process leads to the nanocrystallization firstly along the direction perpendicular to the basal plane of graphite (cuttingly milling), and then parallel to the basal plane (cleavingly milling).

As shown in Figure 1, the total hydrogen concentration increases with decreasing crystallite sizes, accompanying the increase in the number of the defects. The concentration reaches 7.4 mass% ($CH_{0.95}$) after milling for 80 h, and this value is comparable to the hydrogen concentration that can be stored in carbon nano-tubes [1–3], and also in the conventional (super-)

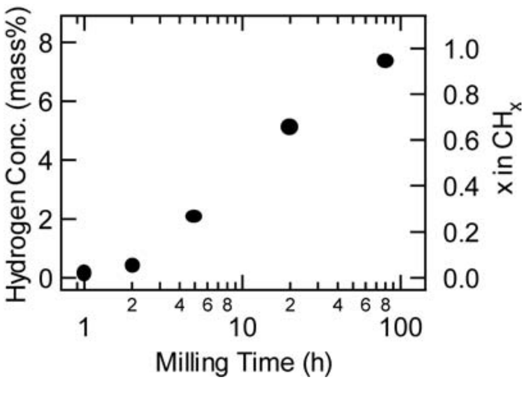

FIGURE 1 Total hydrogen concentration in the nanostructured graphite, as a function of milling time under a hydrogen atmosphere [17,19].

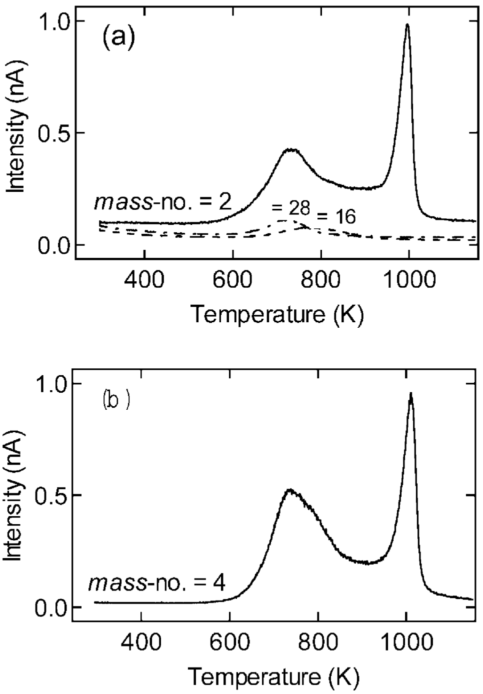

FIGURE 2 Thermal desorption *mass*-spectroscopy of the nanostructured graphite mechanically milled under (a) hydrogen and (b) deuterium atmospheres, respectively [19]. Heating rate was 10 K/min.

activated carbon [20–23] at temperatures below 100 K and hydrogen pressures about 5 MPa.

The specific surface area of the sample after milling for 80 h was only of the order of 10 m^2/g, suggesting that the amount of hydrogen coming from the surface area is rather small compared to the total hydrogen concentration.

The sample obtained after milling for 80 h was also investigated by thermal desorption *mass*-spectroscopy to clarify the dehydriding property of the mechanically prepared nanostructured graphite. The results are shown in Figure 2(a). We found that there are two desorption peaks with *mass*-number = 2, starting at about 600 K and 950 K respectively. These desorption phenomena are also reproducible in the sample mechanically milled under a deuterium atmosphere, as shown in Figure 2(b). This confirms that the hydrogen detected in Figure 2(a) is not coming from adsorbed water or other hydrogen sources, and that it has been surely stored inside the nanostructured graphite. At temperatures around the first desorption peak in Figure 2(a), a small traces of the desorption peaks of hydrocarbons with *mass*-number = 16 from CH_4 and 28 from a fragment of C_2H_6 were also detected. We checked, however, the fraction from the hydrocarbons is only less than 1% in the desorption peak area with *mass*-number = 2 in Figure 2(a). Furthermore, no hydrocarbon has been found at temperatures where the second desorption peak appears.

In our opinion, the first desorption peak in Figure 2(a) has a similar origin as the main desorption peaks of hydrogen from single-walled carbon nanotubes, which has been reported recently by Dillon *et al.* [24] and Hirscher *et al.* [25,26]. (Here the apparent desorption temperatures tend to be modified by "kinetics" effects, depending on the amounts of metallic impurities and heating rates, etc.).

Judging from the results of thermogravimetry, *ca.* 6 mass% of hydrogen, that is 80% of the total hydrogen, is estimated to be desorbed in the first desorption peak in Figure 2(a), as a mixture of *pure* hydrogen and hydrocarbons.

X-ray diffraction profiles after heat-treatments were measured to confirm the recrystallization of the nanostructured graphite around 1000 K. The (002) diffraction peak corresponding to the ordering of the *inter*-layer of graphite can be observed in the sample heated at 1073 K. This is consistent with the above results confirming that the second desorption peak (desorption of residual hydrogen with higher binding energy than that for the first one around 600 K) is related to the recrystallization of the nanostructured graphite. In other words, at temperatures below the second desorption peak, the nanostructured graphite is expected to retain its specific defective structures as suitable trapping sites for hydrogen storage.

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