Hydrogen Absorption and Adsorption Characteristics of Woodceramics

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Hydrogen absorption and adsorption properties of woodceramics, made from radiata pine wood fiberboards carbonized at 923 K and 1473 K, were investigated. The woodceramics carbonized at 923 K absorbed about 0.64 wt.% hydrogen at temperature of 303 K and at an initial hydrogen pressure of 3 MPa, whereas that carbonized at 1473 K absorbed almost no hydrogen. The mean spacing between planar polyaromatic layers of the graphite in the woodceramics carbonized at 923 K slightly increased after hydrogen absorption. Most of adsorbed hydrogen for the woodceramics carbonized at 923 K, at temperature of 100 K, desorbed during heating up to 240 K, and the total amount of adsorbed hydrogen was estimated to be about 2.7 wt.%, although that carbonized at 1473 K was only about 0.2 wt.%. It was indicated that the increase of carbonization temperature, that enhances graphitization of the woodceramics, decreased both the hydrogen absorption and adsorption capacities of the woodceramicas.

Key words: woodceramics, carbonaceous materials, carbonization, hydrogen, absorption, adsorption

1. INTRODUCTION

Woodceramics [1], based on woody materials carbonized at elevated temperatures after impregnating with phenolic resin, have been developed as new kinds of porous carbonaceous materials and belong to one of the ecomaterials that can be made from wood waste materials. Several studies on fundamental as well as practical aspects of the woodceramics have been performed since their development. They have quite good properties for electrical resistance, electromagnetic shielding and infrared radiation, and are being expected to be used in a wide variety of industrial fields, such as wear-resistant materials, heat insulator and infrared radiators, etc [2,3].

On the other hand, some of carbonaceous materials, such as carbon nanotubes [4], carbon nanofibers [5] and nanostructured graphite produced by mechanical milling in hydrogen atmosphere [6] had been reported to absorb great amount of hydrogen. Although there is a sort of controversial disagreement whether they absorb hydrogen or not, much attention is still being directed to hydrogen storage capacities in such carbonaceous materials. In this study, hydrogen absorption and adsorption properties of woodceramics, which were made by carbonizing radiata pine wood fiberboards at temperatures of 923 K and 1473 K, were investigated, aiming to expand their industrial applications.

2. EXPERIMENTAL PROCEDURE

The starting woody material used in this study was medium-density radiata pine fiberboards. These materials were impregnated with phenolic resin, and then were carbonized at two kinds of temperatures of 923 K and 1473 K. The final products are porous carbonaceous materials called "woodceramics". The boards were cut into small samples.

Hydrogen absorption and adsorption experiments for the samples were carried out in a high-pressure vessel, which was made of stainless steel. The vessel containing the sample was evacuated by a rotary pump and then back-filled with pure (99.99999%) hydrogen gas several times, and the final hydrogen pressure was kept to 3 MPa. For the hydrogen absorption experiment, the vessel was heated by an electric heater surrounding the vessel and was kept to a temperature of The hydrogen pressure in the vessel was 303 K monitored by a pressure transducer. For the hydrogen adsorption experiment, on the other hand, the vessel was cooled down to a temperature about 100 K in liquid nitrogen. After maintaining the vessel at a temperature of 100 K for several minutes, the vessel was removed from liquid nitrogen and was heated back to a room temperature. The amount of hydrogen adsorbed was estimated from the pressure increase during heating back to a room temperature from 100 K by a capacitance manometer. The microstructural change of the woodceramics before and after hydrogenation was investigated by X-ray diffraction (XRD) measurement, which was performed by a JEOL JDX-11PA, using Cu Ka radiation at 30 kV and 20 mA.

3. RESULTS AND DISCUSSION

3.1 Effects of carbonization conditions on the structure of the woodceramics

X-ray diffraction patterns for the woodceramics carbonized at 923 K and 1473 K are shown in Fig.1. Both patterns are very similar. The broad X-ray diffraction peaks are observed at about $20\approx25^\circ$ and 45° , which are closely related to the X-ray diffraction peaks obtained from a graphite crystal, for both samples. The first peak corresponds to the 002 diffraction plane of the graphite, and the second one to the 100 and the 101 planes of the graphite, but the diffractions from these two peaks cannot be resolved well in this study, because the degree of the graphitization is poor. Thus, we just indexed the second one as the 10 diffraction plane (the



Fig.1 X-ray diffraction patterns for the woodceramics carbonized at 923 K and 1473 K.

third miler index is missing). Furthermore, any other diffraction peaks generally observed for the typical graphite crystal possessing a high crystallinity cannot be detected, indicating that the local structure of the present woodceramics samples were turbostratic structures. Thus, the planar polyaromatic layers constituting the graphite structure of the woodceramics must laminate in parallel with each other, but their lamination seems to be irregular.

The increases of the carbonization temperature as well as heating rate to reach the carbonization temperature had been reported to increase the dimensional shrinkage and weight loss of the woodceramics [7, 8]. The increase of the heating rate also leaded to the decrease of the compressive and tensile strength [8]. To investigate the effect of additional carbonization treatment at elevated temperatures on the local structures, the samples carbonized at 923 K were annealed in a vacuum. The X-ray diffraction patterns of the woodceramics annealed at 1073 K and 1273 K after carbonization at 923 K are shown in Fig. 2.



Fig.2 The X-ray diffraction patterns of the woodceramics annealed at 1073 K and 1273 K after carbonization at 923 K.



Fig.3 Hydrogen concentration in the woodceramics carbonized at 923 K as a function of hydrogenation time at a temperature of 303 K and at an initial hydrogen pressure of 3 MPa.

The pattern for the sample just after carbonization at 923 K is also included in Fig. 2. The X-ray diffraction intensities of the peaks corresponding to the 002 and the 10 planes of the graphite structure in the samples increase with increasing the annealing temperatures, suggesting that the increase of the carbonization temperature enhances the graphitization of the woodceramics. These results indicated that the carbonization or annealing at higher temperature enhances to grow polyaromatic layers and to order their lamination more regularly. Thus, it is implied that the degree of the graphitization for the sample carbonized at 1473 K is better than that carbonized at 923 K. Although the increase of the carbonization temperature was reported to decrease the 002 interplanar spacing of the crystalline graphite component [8], almost no shifts of the 2θ angle of the 002 as well as 10 plane diffractions can be observed in this study.



Fig.4 X-ray diffraction patterns of the woodceramics carbonized at 923 K and then hydrogenated.



Fig.5 Hydrogen desorption curve after hydrogen adsorption experiments at 100 K for the woodceramics carbonized at 923 K and 1473.

3.2 Hydrogen absorption

Hydrogen concentration in the woodceramics carbonized at 923 K as a function of hydrogenation time is shown in Fig. 3. At a temperature of 303 K and at an initial hydrogen pressure of 3 MPa, the hydrogen concentration level gradually increases and reaches about 0.64 wt.% at hydrogenation time of about 180 h. The activation treatment, sometimes performed to modify the hydrogenation properties for metal hydrides, was not carried out in this experiment. Figure 4 shows the X-ray diffraction patterns of the carbonized at 923 K and then woodceramics hydrogenated. The mean spacing between planar polyaromatic layers (002 interplanar spacing) of the graphite structure in the woodceramics carbonized at 923 K slightly increased after hydrogen absorption, indicating that hydrogen atoms had entered inside the graphite structure, that is between the lamination of the planar polyaromatic layers. It had been reported for nanostructured graphite produced by mechanical alloying that there were two types of hydrogen coordination: hydrogen in the graphite interlayer and at the C-H covalent bond [6].

For the sample carbonized at 1473 K, on the other hand, a clear pressure drop due to hydrogen uptake was not detected, indicating that the sample carbonized at 1473 K absorbed almost no hydrogen. It is suggested that the increase of carbonization temperature, that enhances graphitization of the woodceramics, decreased the hydrogen absorption capacities of the woodceramicas.

3.3 Hydrogen adsorption

The results of the hydrogen adsorption experiments for the woodceramics carbonized at 923 K and 1473 K are shown in Fig. 5 (a) and (b), respectively. For comparison, the data for commercially available graphite powders as well as those without sample in the vessel (blank run) are also included in Fig. 5 (b). Note that the scale of the vertical axis in Fig, 5 (a) is 15 times as large as that shown in Fig. 5 (b). Most of adsorbed hydrogen at a temperature of 100 K for the woodceramicas carbonized at 923 K is desorbed during heating the temperatures up to 240 K. The total amount of desorbed/adsorbed hydrogen was estimated to be about 2.7 wt.% form the pressure change in the vessel.

The adsorbed hydrogen for the sample carbonized at 1473 K, however, is gradually desorbed at temperatures up to room temperature and the total hydrogen adsorbed/desorbed is only about 0.2 wt.%, suggesting that the increase of carbonization temperature, or the increase of the graphitization of the woodceramics, also decreased the hydrogen adsorption capacities of the woodceramicas, similar to the results for hydrogen absorption experiments mentioned earlier. Higher carbonization temperature that enhances to increase the dimensional shrinkage and the weight loss of the woodceramicas [7, 8] must give higher density and less porosity for the woodceramics.

4. CONCLUSIONS

Hydrogen absorption and adsorption properties for woodceramics carbonized at temperatures of 923 K and 1473 K were investigated. The results obtained were summarized as follows.

- The carbonization (or annealing) at higher temperature enhanced to order the lamination of polyaromatic layers.
- The woodceramics carbonized at 923 K absorbed about 0.64 wt.% hydrogen at a temperature of 303 K and at an initial hydrogen pressure of 3 MPa, whereas that carbonized at 1473 K absorbed almost no hydrogen.
- 3. The mean spacing between planar polyaromatic layers of the graphite structure in the woodceramics carbonized at 923 K slightly increased after hydrogen absorption.
- 4. Most of adsorbed hydrogen for the woodceramics carbonized at 923 K, at temperature of 100 K,

desorbed during heating up to 240 K. The total amount of adsorbed hydrogen was estimated to be about 2.7 wt. %, although that carbonized at 1473 K was only about 0.2 wt. %.

5. The graphitization of the woodceramics decreased both the absorption and adsorption capacities for hydrogen.

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