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Micro Pore Structures of Woodceramics Prepared by MDF- and Powder-Methods

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Micro pore structures (specific surface area and micro pore size distribution) of woodceramics prepared by MDF- and powder-methods were examined in relation to the contraction behavior, density change and changes in X-ray diffraction patterns. The contraction percentages and bulk-densities increased remarkably with increasing heating temperature at the temperature range from 400 to 700℃, however, they scarcely changed by heating at the temperature above 700℃. The specific surface areas of these specimens showed maximum values at 700℃ : 450 $m^2 \cdot g^{-1}$ in the specimen containing 70% phenolic resin powder, 380 $m^2 \cdot g^{-1}$ in the specimen containing 30% phenolic resin powder, 300 $m^2 \cdot g^{-1}$ in the MDF specimen and 230 $m^2 \cdot g^{-1}$ in the specimen containing 10% phenolic resin powder. The volume of micro pores with about 0.5 nm diameter increased with increasing temperature from 600 to 700℃, and above 700℃ the volume decreased.

Key words: woodceramics, carbon, phenolic resin, wood powder, micro pore structure, specific surface area

1. INTRODUCTION

Woodceramics (WCS) are new porous carbon materials which were developed for the purpose of the effective use of waste wood [1]. Corresponding to the kind and shape of starting wood materials such as medium density fiber board (MDF) and wood powder, the following two methods are usually used for preparing the WCS [1]. In the first method, the WCS are prepared by carbonizing the MDF impregnated with liquid phenolic resin in a vacuum furnace. In this method, the impregnated phenolic resin changes into hard glassy carbon during carbonizing process and reinforces the soft charcoal which originated from wood fibers in the MDF. In the second method, the WCS are prepared by carbonizing the compacted mixtures of wood powder and phenolic resin powder in a vacuum furnace. In this paper, we call the first method "MDF-method" and the second "powder-method", and also we abbreviate the specimen prepared by the first method to "MDF-(method) specimen" and that prepared by the second method to "powder-(method) specimen".

It has been reported that the WCS prepared by the MDF-method have superior mechanical properties [2], wear properties [3], electrical properties [4], electromagnetic shielding properties [5], electromagnetic wave absorption properties [6] and gas adsorption properties [7],[8]. However, the micro pore structure of the MDF-method specimen has been scarcely reported. On the other hand, the absorption and adsorption characteristics of the powder-method specimen also have been scarcely reported.

Therefore, in this study, micro pore structures (specific surface areas and micro pore size distributions) of the MDF- and powder-method specimens were clarified in relation to the contraction behaviors, density changes and changes in X-ray diffraction patterns.

2. EXPERIMENTAL

The powder-method specimens used in this study were made by the following processes. First, the starting mixtures of the compositions shown in Table 1 were compacted into tetragonal shape at the pressure of 100 MPa at room temperature and then heated under low vacuum (8 kPa) in an electric furnace for 4h at the several temperatures : 400, 500, 600, 700 and 800℃.

Table 1 Compositions of starting mixtures for powder-method specimens (mass%).

No.	Phenolic resin powder	Wood powder
A	10	90
B	20	80
C	30	70
D*	50	50
E*	70	30
F*	100	0

*swelled out

The heating speed was 1 ℃/min. The length, volume, weight and bulk density were measured for the tetragonal shape specimens heated at each temperature. The specimens D, E, and F were swelled out by heating and therefore could not measured. The MDF-method specimens were prepared by heating the phenolic resin impregnated medium density fiber boards (phenolic resin content : 33%) , received from Tohoku System Inc., at 400-800 ℃ for 4 h in the same way as the powder-method specimens.

The specific surface areas of these specimens were measured using an adsorption system,"BELSORP-mini", produced by Bel Japan Inc. In this experiment, nitrogen gas was used as the adsorbate and the adsorption isotherm (isothermal adsorption curve) at 77.4 K was measured. Then the specific surface area was calculated by using BET method [9] and the micro pore size distribution was obtained by MP method [10].

The scanning electron microscopic (SEM) observation and X-ray diffraction analysis (λ : CuK_{α}) were also performed.

3. RESULS AND DISCUSSION

Figure 1 shows the contraction behaviors (in length) of the MDF- and powder-method specimens.

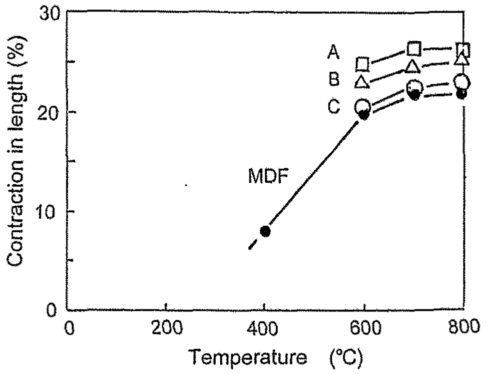

Fig.1 Contraction behavior of woodceramics specimens prepared by MDF- and powder-methods during heating.

The MDF-method specimen contracted remarkably by heating from 400 to 700℃ and then kept the nearly constant value (about 22%) above 700 ℃ . The powder-method specimens contracted in the nearly same manner as the MDF-specimen on heating from 600 to 700℃ and then kept the nearly constant values above 700℃. The contraction percentages of these C, B and A specimens at 800℃ were 23, 25 and 27%, respectively.

Figure 2 shows the bulk density changes of the MDF- and powder-method specimens with heating from 600 to 800℃. The bulk densities of all specimens increased by heating below 700℃ and kept the nearly constant values above 700℃. The bulk densities of MDF, C, B and A at 800℃ were 0.88, 0.83, 0.78 and 0.73 g・cm-3, respectively.

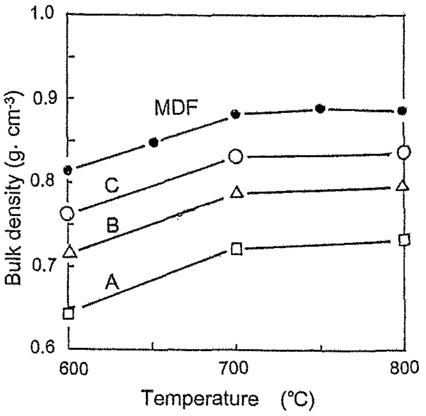

Fig.2 Changes in bulk density of woodceramics specimens prepared by MDF- and powder-methods during heating.

Figure 3 shows the microstructures at the cross sections of woodceramics specimens heated at 600℃ observed using SEM. The specimen A, which was prepared by heating the compacted mixture of 10% phenolic resin powder and 90% wood powder, shows the complicated structure originated from the combination of wood and phenolic resin powders as observed in Fig 3(a). The specimen C shows the simple structure consists of the matrix (M) and macro pores (arrowhead P) as observed in Fig 3(b). The MDF specimen (c) shows the similar structure to the specimen C. Its structure consists of many ducts in wood fibers (arrowhead D) and macro pores (arrowhead P). The structures of all specimens scarcely changed by heating to 700 and 800℃.

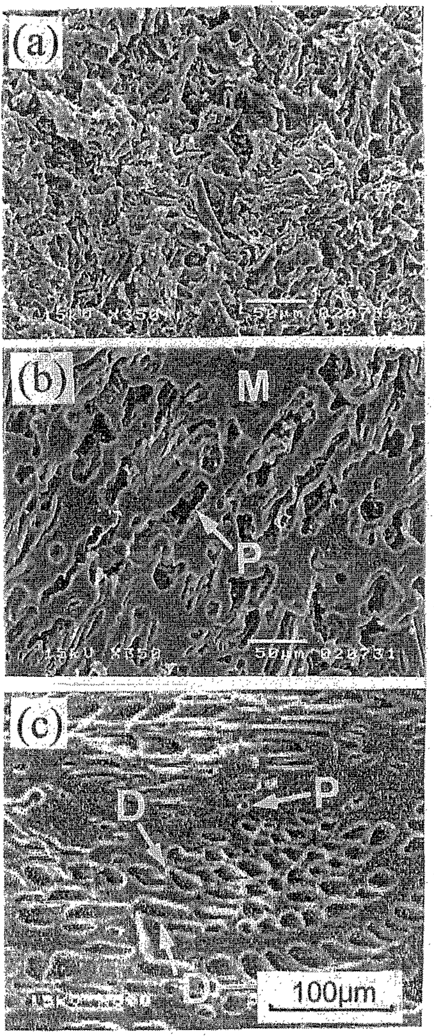

Fig.3 SEM microstructures at the cross sections of woodceramics specimens heated at 600℃. (a) A specimen, (b) C specimen and (c) MDF specimen.

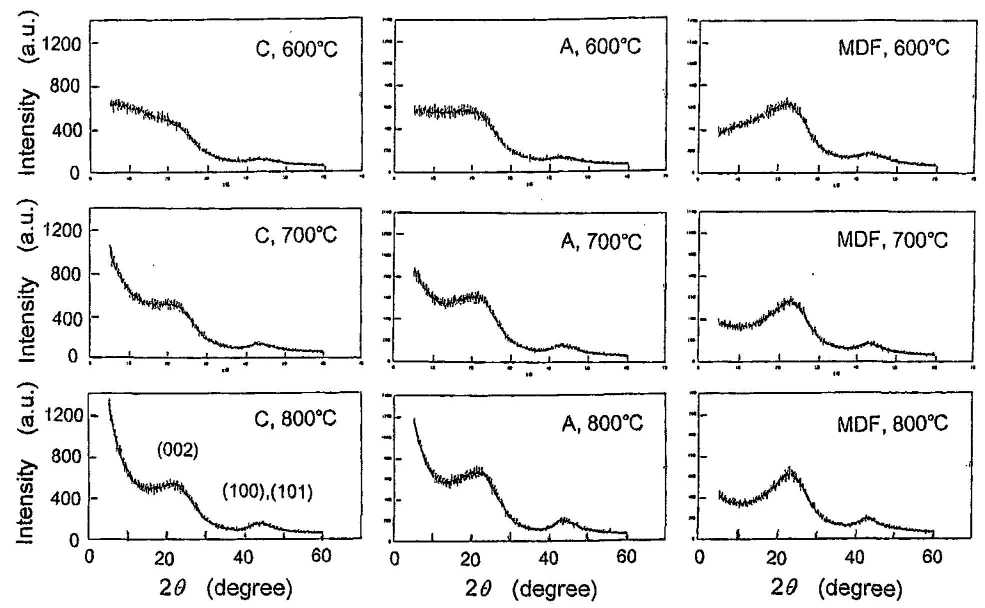

Fig.4 Changes in X-ray diffraction patterns of woodceramics specimens prepared by MDF- and powder-methods with increasing temperature.

Figure 4 shows the changes in X-ray diffraction patterns of C, A and MDF specimens with increasing temperature. The graphite (002) peak and graphite (100)/(101) peak of each specimen were broad, however these peaks became sharp and shifted to higher angle with increasing heating temperature. This facts means that each specimen had the amorpous carbon structure containing graphite crystallites (micro graphites) and the interplanar spacings of these (002) and (100)/(101) planes of crystallites became narrow with increasing temperature.

Figure 5 shows the changes in interplanar spacing d_{002} of woodceramics specimens C, A and MDF with increasing temperature. The interplanar spacing d_{002} of the C specimen changed from 0.430 to 0.400 nm, that of the A specimen changed from 0.420 to 0.390 nm and that of the MDF changed from 0.396 to 0.380 nm.

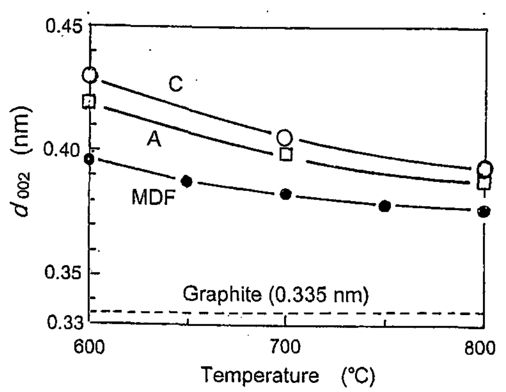

Fig.5 Changes in lattice spacing d_{002} of woodceramics specimens C, A and MDF with increasing temperature.

Figure 6 shows the adsorption isotherms at 77.4 K (-195.8℃) of nitrogen for specimen A heated at 600, 700 and 800℃. All specimens adsorbed nitrogen rapidly at the low relative pressure below 0.1 and then adsorbed slowly with increasing relative pressure. The other specimens (C, B and MDF specimens) also showed similar curves to those of A. These curves belong to the type I in the classification by Brunauer, Deming, Deming and Teller (BDDT classification) [11], namely the Langmuir adsorption type [12].

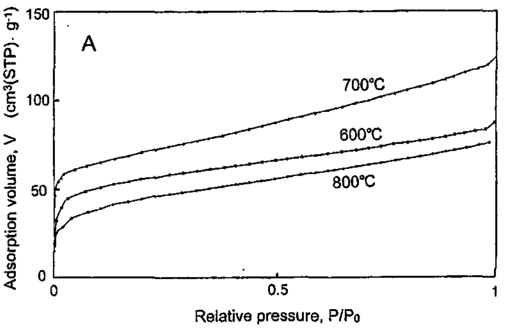

Fig.6 Adsorption isotherms of nitrogen at 77.4 K (-195.8 ℃) for the specimen A heated at 600-800℃.

Figure 7 shows the specific surface areas of MDF- and powder-method woodceramics. These results obtained from the BET plots [9] of the adsorption isotherms of each woodseramics specimen as shown in Fig.6. This specific surface areas of all specimens increased with increasing temperature from 600 to 700℃ and then decreased with increasing temperature from 700 to 800℃. The maximum specific surface areas of these specimen at 700℃ were 380 m^2 · g^{-1} for specimen C, 300 m^2 · g^{-1} for MDF specimen and 230 m^2 · g^{-1} for specimen A.

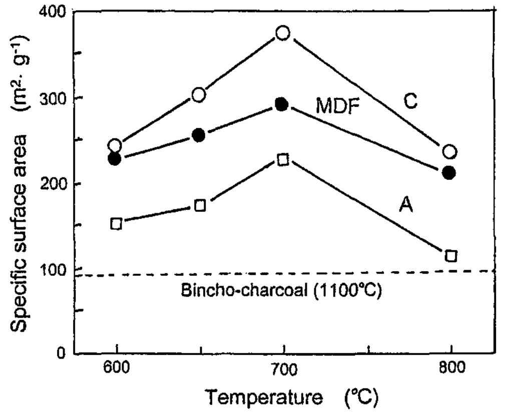

Fig.7 Changes in specific surface area of woodceramics specimens prepared by MDF- and powder-methods with increasing heating temperature.

Figure 8 shows the micro pore size distributions of MDF- and powder-method specimens (C, MDF and A). The volume of micro pores with about 0.5 nm diameter increased with increasing temperature between 600 and 700℃ in all specimens. However, avobe 700℃, the volume of these micro pores decreased with increasing temperature.

Figure 9 shows the specific surface areas of the powder-method specimens. The maximum specific surface area, 450 $m^2 \cdot g^{-1}$, was obtained in the specimen E (70% phenolic resin). The specific surface area of the specimen (E) containing 100% phenolic resin was nearly equal to that of the specimen (A) containing 10% phenolic resin.

In general, the structural change of the organic materials with heating under vacuum or non-oxidative conditions progresses through two main processes, namely the carbonization and graphitization [13]. The carbonization process, which includes the aromatization,

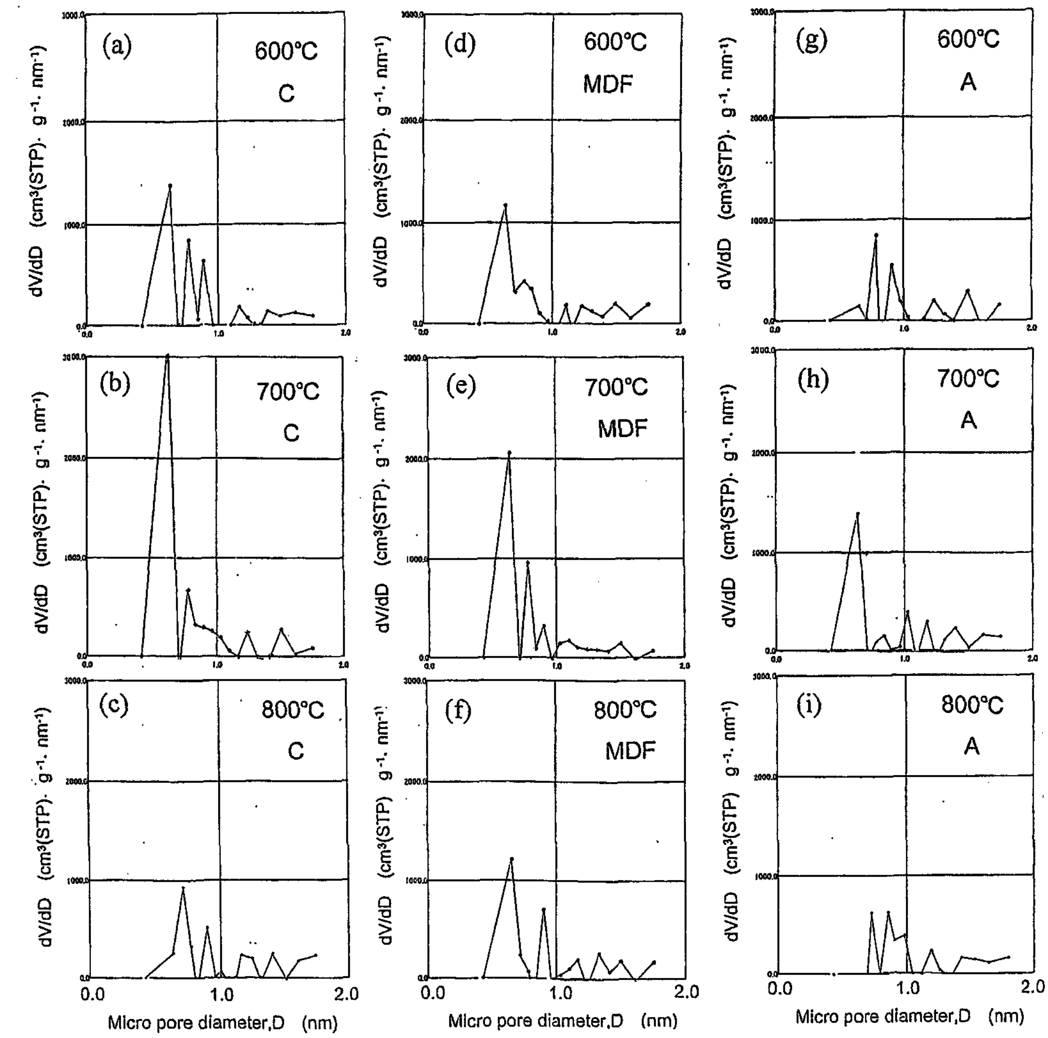

Fig.8 Micro pore size distrubutions of woodceramics specimens prepared by MDF- and powder methods.

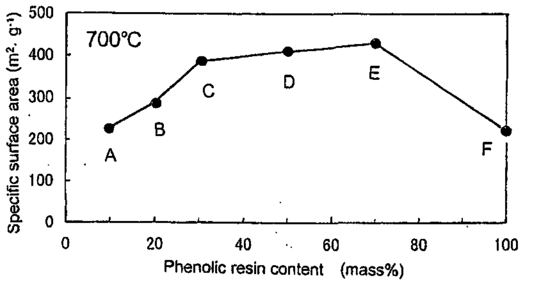

Fig.9 Specific surface areas of powder-method specimens heated at 700℃.

dehydrogenative condensation and formation of graphite crystallite (micro graphite) with 3-4 layers of hexagonal aromatic rings structure, starts from relative low temperatures such as 200 or 300℃ and lead to the contraction of the specimen. The subsequent graphitization process, which means the process of the three dimensional growth of the graphite crystallite, namely the growth of the graphite crystallite along the a and b axes and the decrease in distance along the c axis between graphite crystallites (corresponding to the micro pore diameter shown by arrowhead in Fig.10(a)), progresses from relative high temperatures such as 600 or 700℃. In this study, all specimens prepared from MDF and powder contracted with heating below 700℃. Therefore, it seems that the above carbonization process progressed in all specimens with heating below 700℃. However, the arrangement and distribution of graphite crystallites may be different among the specimens; namely the specimen A containing a lot of charcoal originated from wood powder probably has the similar structure to that shown in Fig.10 (a) and the specimen C containing more quantity of the non-graphitizing carbon originated from phenolic resin powder probably has the similar structure to that shown in Fig. 10 (b). As a result, the specific surface area and the volume of micro pores (arrowheads in Fig.10) with about 0.5 nm diameter increased with increasing phenolic resin content as shown in Figs.7-9. On the other hand, with increasing temperature above 700℃, the graphitization process mainly progressed and the mean distance (micro pore diameter) between graphite crystallites decreased. As a result, the volume of micro pores with about 0.5 nm diameter decreased avobe 700℃ as shown in Fig.8 and the specific surface areas decreased above 700℃ as shown in Fig.7.

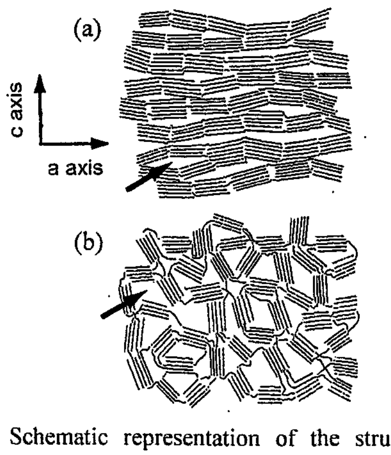

Fig.10 Schematic representation of the structures of graphitizing carbon (a) and non-graphitizing carbon (b) proposed by Franklin [14]. Arrowheads show micro pores.

One of reasons why the specific surface area of 100% phenolic resin specimen (F) is smaller than that of the specimen containing 70% phenolic resin (E) as shown in Fig.9 may be attributed to the lack of macro pores, through which the adsorption gas (N_2) can be introduced into micro pores, because the 100% phenolic resin specimen have no graphitizing carbon (charcoal) with larger quantity of macro pores originated from ducts in wood powders.

4. SUMMARY

Micro pore structures (specific surface area and micro pore size distribution) of woodceramics prepared by MDF- and powder-methods were examined. The specific surface areas of these specimens showed maximum values at 700℃, namely 450 $m^2 \cdot g^{-1}$ in the specimen containing 70% phenolic resin, 380 $m^2 \cdot g^{-1}$ in the specimen containing 30% phenolic resin, 300 $m^2 \cdot g^{-1}$ in the MDF specimen and 230 $m^2 \cdot g^{-1}$ in the specimen containing 10% phenolic resin, respectively. The volume of micro pores with about 0.5 nm diameter increased with increasing temperature from 600 to 700℃, however, above 700℃ the volume decreased.

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