Transactions of the Materials Research Society of Japan 29[5] 2515-2518 (2004)

Evaluation of Waterproof Property of Woodceramics

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Waterproof property of woodceramics carbonized at from 650℃ to 1200℃ was evaluated from a physical and chemical viewpoint. The waterproof ability of the 800℃ carbonized woodceramics was low because of swell due to water absorption by the remained hydroxyl groups. On the other hand, the waterproof ability of the 1000℃ carbonized woodceramics was improved because the elimination of hydroxyl groups in the woodceramics was accelerated by carbonization at high temperature. However, the strength of 1200℃ carbonized woodceramics decreased a little after soaking-drying processes. The reason is considered as follows; micro-pores within woodceramics shrink remarkably during carbonization at 1200℃. Water which penetrated into the materials during the soaking process vaporizes during drying process. However, shrunken micro-pores retard the vaporization, resulting in the occurrence of internal stress. The decrease in strength of woodceramics carbonized at 1200℃ should be ascribed to the residual stress.

Key words: Woodceramics, porous carbon material, waterproof, carbonization temperature, hydroxyl group

1. INTRODUCTION

Woodceramics is porous carbon material which is fabricated by carbonization after impregnating phenolic resin into woody material. In generally, woodceramics is known as a recyclable multiple materials.

Now, various experiments have been carried out toward the practical use of woodceramics, however, a present problem is the strength reduction of woodceramics when it contacts with water.

In the previous report, strength of woodceramics decreased by contact with water when the waterproof property of woodceramics carbonized at from 650℃ to 800℃ were evaluated [1]. The one of the reasons for strength reduction is that the hydroxyl groups existed in the molecular structure of cellulose and hemicellulose which are the constituents of woody material remains in woodceramics carbonized at lower than 800℃, and these improve hydrophilic nature of woodceramics. Since the hydroxyl groups accelerate water absorption, the carbonized woody material swells by water absorption and the stress is generated between carbonized phenolic resin and carbonized woody material. The macroscopic cracks generate due to the internal stress cause the decrease of the strength. Thus, the purposes in this report is the improvement of the waterproof property through eliminating of hydroxyl groups by the carbonization at higher temperature and the discussion of the strength reduction mechanism taking molecular structures derived from the results of chemical analysis into account.

2. EXPERIMENTAL PROCEDURE

2.1 Specimen

MDF (Medium Density Fiberboard: Noda) and liquid phenolic resin (Honen Co.) were used for raw materials of the woodceramics used in this experiment. First process of fabricating the specimens is impregnating the phenolic resin into the MDF at room temperature by pressure reduction method. After that, the woodceramics boards were fabricated by carbonizing those raw materials at 650℃, 800℃, 1000℃, and 1200℃ in a vacuum furnace. The 750℃ carbonized MDF without impregnation of phenolic resin was prepared. The boards of woodceramics and the carbonized MDF (hereinafter referred to as "C-MDF") were cut into tetragonal shape peaces of $9 \times 9 \times 18 mm^3$ by a commercially used cutter. Those woodceramics were used as the specimens.

2.2 Repeated Soaking-Drying Test

In order to research of waterproof property of woodceramics, Repeated Soaking-Drying Test (hereinafter referred to as "RSD-Test") was carried out. The test is carried out as follows; the specimens were soaked into purified water and dried down. This process was repeated from 0 to 40 times. Then, compressive stress was applied to the woodceramics along laminating direction of woodfibers which is the lowest strength direction. Figure 1 shows the process in detail. The waterproof property of woodceramics was compared between woodceramics in each carbonized at various temperatures.

2.3 Observation of Longitudinal-Sections

The longitudinal-sections of woodceramics was observed by SEM (Scanning Electron Microscope). The averages of larger pore diameter were obtained from micrographs, and the effects of carbonization temperature on pore diameter were compared each other.

2.4 Chemical Analysis

In order to estimate the amount of remained hydroxyl groups, the elemental analysis were carried out by EDS (Energy Dispersive X-ray Spectroscopy) under nitrogen atmosphere. In addition, molecular structure of woodceramics was estimated by FT-IR (Fourier transforms infrared spectroscopy). From these results, the waterproof property of woodceramics obtained in RSD-Test was discussed.

3. RESULTS AND DISCUSSION

3.1 Evaluation of Waterproof Property by Physical Tests

Figure 2 shows the results of the RSD-Test. The transverse axis shows the repeat count of soaking-drying n. The longitudinal axis of Fig.2(a) shows value of compressive strength σ, and the longitudinal axis of Fig.2(b) shows normalized compressive strength which was obtained by dividing each compressive strength of the repeated soaking-drying specimens σ_n by the compressive strength of non-soaked ones σ_0.

The compressive strength increased as increasing carbonization temperature because of the acceleration of graphitization for woody material and acceleration of transformation of the phenolic resin to glassy carbon.

Besides, strength of the carbonized MDF without impregnation of phenolic resin was lower than that of woodceramics. Consequently, the strength of woodceramics depends on the content of phenolic resin impregnated in woody material and the carbonization temperature.

While the carbonized MDF at 750℃ did not weaken by the soaking-drying processes, the woodceramics which were carbonized at 650℃ or 800℃ weakened little by little, and finally the strength fell over 10% after 40 times of soaking-drying. On the other hand, the woodceramics which were carbonized at 1000℃ or 1200℃ weakened little by the process due to acceleration of elimination the hydroxyl groups. For the woodceramics carbonized at 1000℃, the strength unchanged by contact with water.

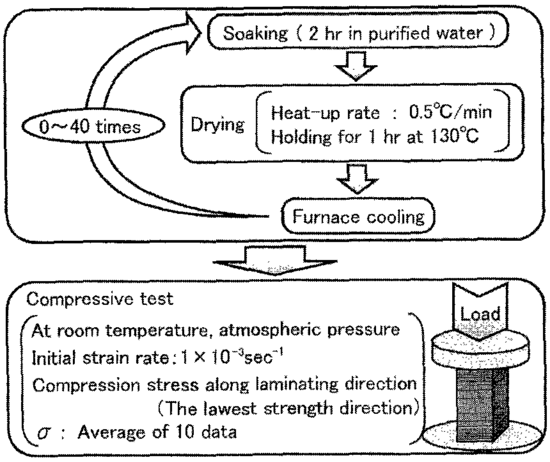

Fig.1 Details of RSD-Test.

Figure 3 shows Weibull modulus m and the average $\bar{m}$ of the Weibull modulus m from RSD-Test. Weibull modulus indicates the variation in measurement data of RSD-Test and high value of Weibull modulus means low variation in measurement data. A value of Weibull modulus of a general ceramics material shows about from 10 to 20 and that of a metal material shows over 100.

The variation of measurement data of the woodceramics was higher than that of C-MDF without impregnation phenolic resin because of cured phenolic resin of uneven impregnation.

In general, it is difficult to impregnate phenolic resin into MDF. Araki reported [2] that the value of Weibull modulus for compressive strength of the 800 ℃ carbonized woodceramics was 4.7. In this experiment, the value moved up to 8.9 for the woodceramics under the same measurement condition due to the improvement of the raw material and impregnation method. Although the value of Weibull modulus was improved, it was too precarious to be used as a practical material. More

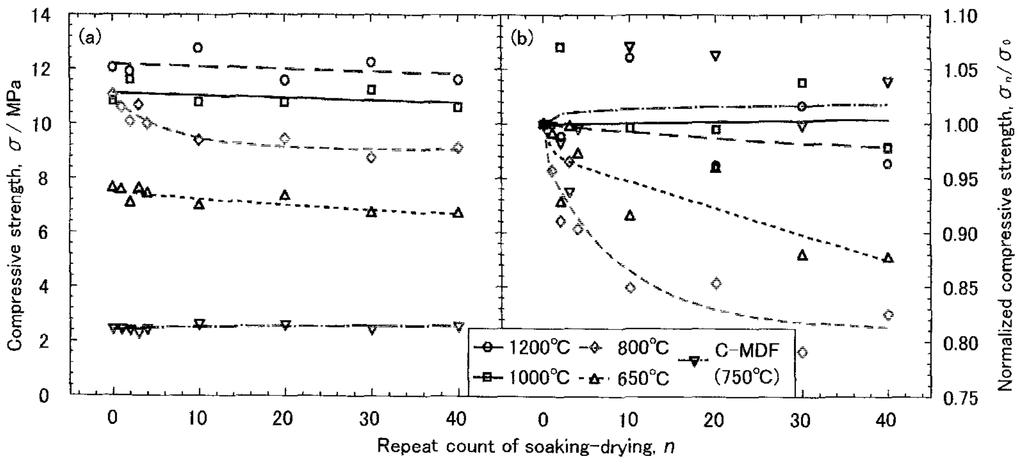

Fig.2 (a) Relationship between the repeat count of soaking-drying n and the compressive strength σ from RSD-Test. (b) Relationship between the repeat count of soaking-drying n and the normalized compressive strength σ_n / σ_0.

improvement is still needed.

The average of Weibull modulus for the compressive strength of 650℃ carbonized woodceramics was lower than that of higher temperature carbonized woodceramics. This result may account as follows; the carbonization of woody material starts around 650℃ and the molecular structure of the material is distributed unhomogeneously. So the values of strength were scattered.

On the other hand, it was confirmed that repeat count of soaking-drying has no relevance to Weibull modulus of compressive strength. The fact suggests that the cracks which occurred by soaking were distributed uniformly in all over the material and penetrate so that these cracks did not become a factor of stress concentration during the compression test.

Figure 4 shows the SEM micrographs of carbonized woodceramics. Figure 5 shows pore diameter φ which was measured on the micrographs. Any micrograph of C-MDF was not able to be taken because the powder dust generated at the process of making the specimens for the SEM observation.

For the woodceramics which was carbonized at under 1000℃; as the carbonization temperature increased, the pore diameter became small. However, the pore diameter of 1200℃ carbonized woodceramics was almost the same as that of 1000℃ carbonized one. The most likely explanation is that the complete finish of volume shrinkage of woodceramics by the termination of carbonized reaction up to 1000℃.

3.2 Evaluation of Waterproof property by Chemical Tests

Figure 6 shows oxygen content ratio of the woodceramics and the C-MDF which were measured by EDS. For 650 ℃ carbonized woodceramics to 1000 ℃ carbonized woodceramics; as the carbonization temperature increased, the oxygen content ratio decreased. However, about 1200℃carbonized woodceramics; as the carbonization temperature increased, the oxygen content ratio also increased. On the other hand, for the oxygen content ratio of C-MDF fabricated at 750℃ was 5% lower than the curve of oxygen content ratio of woodceramics.

It is reported that hydroxyl groups does not remain completely in the woodceramics which was carbonized over 1000℃. However, the volume of oxygen content ratio was 17% in the 1000℃ carbonized woodceramics. It exceeds drastically the theoretical value supposed from the molecular structure. The cause of this result is thought to be aftereffects of the H_2O and CO_2 in the air which were absorbed to the pores physically as well as the remained hydroxyl groups. Woody material has porous structure by nature. In addition, phenolic resin emits gas during the cure and the traces of gas emitting remain in woodceramics. Therefore, the amount of absorption gas for woodceramics is greatly higher than that for charcoal. Consequently, the quantitative analysis of the remained hydroxyl groups of woodceramics by EDS is difficult because of the physical absorption.

The reduction of oxygen content ratio in the woodceramics carbonized at under 1000℃ as increase of carbonization temperature is caused by the

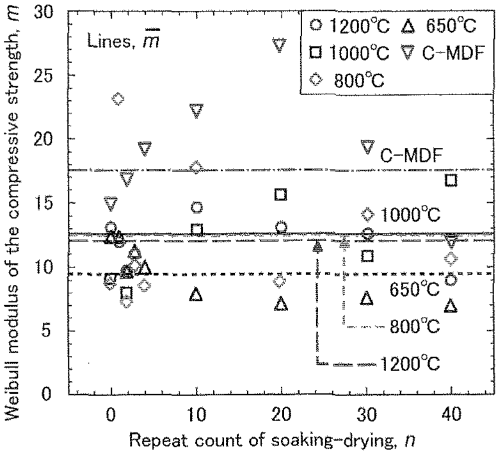

Fig.3 Relationship between the repeat count of soaking-drying n and Weibull modulus m and the average $\bar{m}$ of the Weibull modulus from RSD-Test.

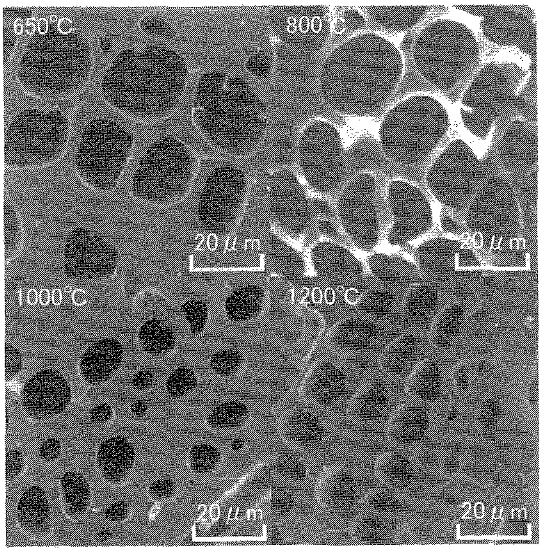

Fig.4 SEM micrographs of the longitudinal-sections of woodceramics carbonized at various carbonization temperatures.

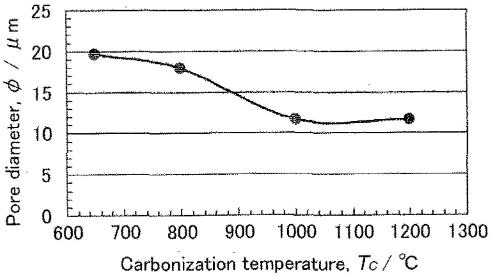

Fig.5 The pore diameter φ of woodceramics obtained from the SEM micrographs.

elimination of hydroxyl groups as acceleration of carbonization reaction for woody material and phenolic resin at high temperature, and reduction of the H_2O absorption.

The increase of oxygen content ratio of 1200℃ carbonized woodceramics is caused by the pore shrinkage due to graphitization of woody material and phenolic resin. As it mentioned before, the carbonization reaction of woodceramics had almost finished at over 1000℃. However, the shrinkage of macro or micro pores which were too small to be observed by SEM had not finished yet. And the molecules of H_2O and CO_2 physically absorbed at the pores were prevented to vaporize to outside.

Figure 7 shows IR spectra for the woodceramics and C-MDF. In the all spectra, peak around 3450cm^{-1} was observed. That was associated with the remained hydroxyl groups and the chemically and physically absorbed H_2O from the air. The peak around 1630cm^{-1} was associated with the absorbed CO_2 from the air. Besides, around 2920cm^{-1}, the peak was observed in only 650℃ carbonized woodceramics and associated with alkyl groups due to insufficient elimination of the hydrogen atoms during the carbonization reaction. On the other hand, the small peak was observed around 2360cm^{-1} in 800℃ carbonized woodceramics and 750℃ C-MDF. This was observed irrespective of impregnation of phenolic resin. Thus, this peak is associated with triple bond of carbon elements during graphitization of woody material.

4. SUMMRY

The compressive strength of woodceramics increased as carbonization temperature increase because of the accelerations of graphitization of woody material and the transformation of phenolic resin into grassy carbon. For 650℃ carbonized woodceramics, its variation of the compressive strength fell off because of the unfinished carbonization reaction and its unsteady molecular structure. Waterproof property of 650℃ carbonized woodceramics and 800℃ carbonized one was lower because of remained hydroxyl groups. The compressive strength of 1000℃ carbonized woodceramics, in contrast, did not reduce in spite of contacting with water because elimination of hydroxyl groups in the woodceramics was accelerated by the high temperature. However, the strength of the 1200℃ carbonized woodceramics decreased a little after 40 times of RSD-Test. It is may account for the remarkable shrinkage of micro-pores unobserved by SEM within woodceramics during carbonization at 1200℃. Water which penetrated into the materials in the soaking process vaporizes during drying process. However, above-mentioned micro-pores retard the vaporization, resulting in the occurrence of internal stress. The strength of the 1200℃ carbonized woodceramics should be decreased due to the effect of residual stress. Besides, it was indicated that the detection of remained hydroxyl groups is difficult because of the influence of physical adsorption of H_2O and CO_2 on woodceramics.

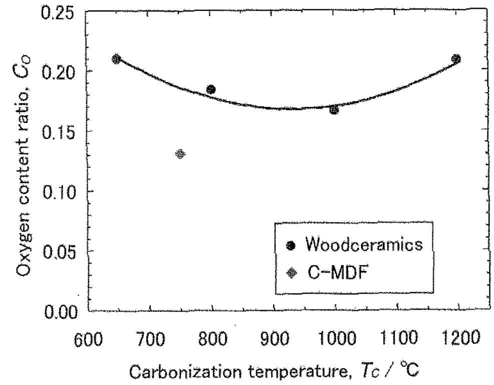

Fig.6 Oxygen content ratio C_O of woodceramics and C-MDF by EDS.

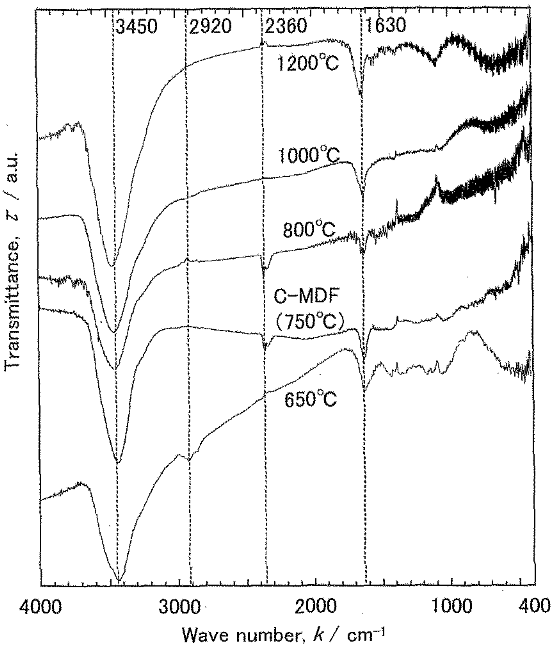

Fig.7 IR spectra of woodceramics and C-MDF.

REFERENCES

[1] T. Mikamo, K. Ogawa, M. Otsuka and T. Okabe, Transactions of the Materials Research Society of Japan, **28**, 1087-1090, (2003).

[2] Syunji Araki, *Thermal shock resistance and mechanical reliability of woodceramics.*, master's thesis, Shibaura Inst. of Tech., 25-31, (1998)

(Received October 11, 2003; Accepted December 11, 2003)