

# CARBONIZATION OF WOOD-SILICA COMPOSITES AND FORMATION OF SILICON CARBIDE IN THE CELL WALL

*Takeshi Furuno*

Professor

and

*Masashi Fujisawa*<sup>1</sup>

Graduate Student

Faculty of Science and Engineering

Shimane University

Matsue, Shimane 690-8504, Japan

(Received August 2003)

## ABSTRACT

Wood-mineral composites (WMCs) impregnated with silica ( $\text{SiO}_2$ ) were carbonized at high temperature to form silicon carbide (SiC) directly using carbon from the wood with the impregnated silica. Carbonized composites were investigated using X-ray diffraction and EPMA (electron probe X-ray microanalysis). Water-saturated sapwood specimens of sugi, Japanese cedar (*Cryptomeria japonica*), were diffuse-penetrated with a colloidal silica solution or a water glass solution followed by drying to fix silica gel for preparing wood- $\text{SiO}_2$  composites. The composites were burned at 600°C, 1000°C, and 1300°C for 30–120 minutes in a furnace in nitrogen gas. X-ray diffraction showed that the peak of  $\text{SiO}_2$  was recognized at  $2\theta = 22^\circ$ , and the peak became greater with an increase in burning temperature. The peak at 1300°C became very sharp, revealing the change of crystalline structure of  $\text{SiO}_2$  (cristobalite). In addition, the occurrence of the peak around  $2\theta = 35^\circ$  at 1300°C appeared, which confirmed the formation of silicon carbide ( $\beta$ -SiC) in the carbonized composites. EPMA observation showed the distribution of silicon in the cell walls that were carbonized at 1300°C. In conclusion, we showed that SiC was produced in the cell walls and the crystalline structure-changed  $\text{SiO}_2$  (cristobalite) existed in the cell lumina.

*Keywords:* Carbonization, wood-silica composite, silicon carbide, cristobalite, X-ray diffraction, EPMA.

## INTRODUCTION

Charcoal obtained by heating wood in the absence of air has an excellent porous structure derived from the wood anatomy. Accordingly, recent research on the utilization of charcoal and the carbonization of wood has been reported extensively (e.g., Abe 1996; Ishihara 1997; Yatagai 1997; Byrne and Nagle 1997; Kitamura et al. 1999; Kitamura and Katayama 2001; Kitamura et al. 2002).

In the field of ceramics, a biomimetic process has attempted to produce novel materials; that is, production of ceramic wood by mimicking fossil wood (Ota et al. 1995a, 1995b, 1997, 1998).

Their work investigated the possibility of reproducing the structure of wood in a ceramic. The porous structure in wood makes it an attractive template for special porous ceramics such as catalyst supports, machinable ceramics, light structural and tough ceramics, low thermal conductive ceramics, and others.

Thus far, the authors have been studying wood-mineral composites (WMCs) using the water glass-boron compound system and the colloidal silica solution system to enhance properties such as dimensional stability, fire resistance, decay resistance, termite resistance, bending strength, and other mechanical qualities (Furuno et al. 1993, 1995, 1996, 1997; Furuno and Imamura 1998; Furuno et al. 1999, 2001).

In this research, we investigated the possibility of producing a novel material by carbonizing

<sup>1</sup> Presently doctoral student at Wood Research Institute, Kyoto University, Uji, Kyoto 611-0011, Japan.

wood composites impregnated with silica. The formation of silicon carbide (SiC) was accomplished by directly utilizing the carbon from the wood together with impregnated silica during the carbonization process. Subsequently, the state of carbonization and the presence and location of SiC in carbonized composites were investigated by X-ray diffraction and EPMA (electron probe X-ray microanalysis).

Research on the formation of SiC in wood ceramics was limited. It was reported that SiC ceramics with the original wood structure were produced by vacuum-infiltrating charcoal with tetraethyl orthosilicate (Ota et al. 1995a, 1995b, 1998). Greil and others (Greil et al. 1998a, 1998b; Greil 2001) studied the processing of cellular ceramics with anisotropic pore structures by infiltration of liquid silicon into carbonized wood. They also investigated the mechanical properties of silicon carbide ceramics. In addition, compressive mechanical behavior of biomorphic silicon carbide ceramics was examined, which were fabricated by the infiltration of molten silicon into carbonized wood (Martínez-Fernández et al. 2000). However, the carbonization of wood-silica composites impregnated with colloidal silica or water glass, not using charcoal as a starting material, and the formation of silicon carbide in the composites have not been reported extensively in the literature.

#### MATERIALS AND METHODS

##### *Wood specimens and impregnation*

We impregnated sapwood cubes (10 (L)×10 (R)×10 (T) mm) of Japanese cedar, sugi (*Cryptomeria japonica* D. Don), with an aqueous solution of colloidal silica (30.4% silicic acid anhydride) or water glass (30% silicic acid anhydride) using the diffusion-penetrated process (Furuno and Imamura 1998; Furuno et al. 1997). Three wood specimens were used for each treatment to prepare wood-mineral composites (WMCs). The water-saturated specimens were soaked in the colloidal silica or water glass solutions under atmospheric pressure at 50°C or room temperature for 24 h. The water glass-

impregnated specimens were soaked further in a 5% acetic acid solution at room temperature for 1 h to precipitate silica from silicic acid ions in the alkaline solutions. The specimens impregnated with colloidal silica and water glass solutions were dried at 60°C for 24 h and then dried at 105°C for 24 h to fix firmly silica gel in situ in the wood. Subsequently their oven-dried weights and volumetric sizes were measured to determine weight percent gains (WPGs) of WMC specimens.

##### *Method for carbonization*

For carbonizing WMC specimens, the thermal balance equipment with a large capacity (SINKU-RIKO: TG-7000VHT) was used, which can measure continuously the weight change of the specimens controlling the carbonizing temperature and atmosphere of a sample chamber in the gaseous flow.

The specimens were burned at 600°C, 1000°C, and 1300°C for 30–120 min with the raising rate of 30°C/min in the chamber in an atmosphere of nitrogen gas (flow rate of 1.0 l/min). The holding times for carbonization were 30 min for 600°C and 1000°C, and 30, 60, and 120 min for 1300°C.

##### *X-ray diffraction and observation with EPMA*

Carbonized specimens of the composites were crushed into powder and analyzed by an X-ray diffractometer (PHIRIPS: PW3050) to obtain X-ray diffraction patterns. The conditions for diffraction are as follows: voltage 40kV, electric current 40mA, wavelength 1.518Å (CuK $\alpha$ ), time interval 0.5 s, scanning speed 0.04° s, and coverage of diffraction angle (2 $\theta$ ) 5°–80°.

Transverse surfaces of carbonized specimens, cut by a razor blade from the central portion of each specimen, were coated with gold in vacuo using an ion sputter and they were examined by EPMA (electron probe X-ray microanalysis) (JEOL: X-ray microanalyzer JXA733). The cellular structure of the carbonized specimens and the presence and location of silica were observed with secondary electron images. Furthermore,

the detection and distribution of silicon in the cell lumina as well as cell walls were inspected with X-ray maps.

## RESULTS AND DISCUSSION

### *Weight loss and volumetric shrinkage of carbonized WMC specimens*

Figure 1 shows an example of the relationship between temperature or weight loss and burning time for an untreated wood specimen. The curves of weight loss usually demonstrate abrupt decreases at the initial time in both untreated wood and WMC specimens. Thereafter, the curves are nearly at a constant value. The rate of temperature increase was very important for carbonization. When the rate was too fast (at 115°C/min), the cellular structure of carbonized specimens abnormally shrunk and deformed, as typically shown in Fig. 2. Therefore, the burning rate was fixed at 30°C/min in the experiment.

The weight percent gains (WPGs) of wood-mineral composites (WMCs) as well as the weight loss and volumetric shrinkage of carbonized untreated wood and WMC specimens at different burning temperatures are shown in Table I.

The weight loss (WL) and volumetric shrinkage (VS) of carbonized untreated wood (charcoal) specimens were 74–76% and 55–63%, respectively. These values were not much influenced by burning temperature. On the other hand, carbonized WMC specimens showed the

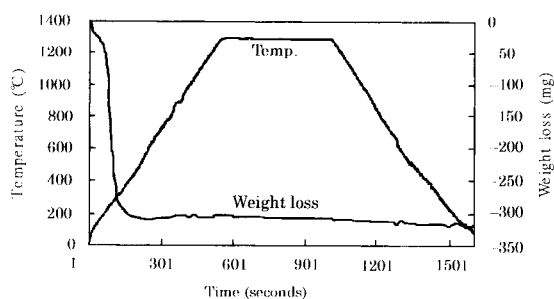


FIG. 1. The relationship between temperature or weight loss and burning time for an untreated wood specimen burned at 1300°C with a raising rate of 30°C/min in the thermal balance equipment.

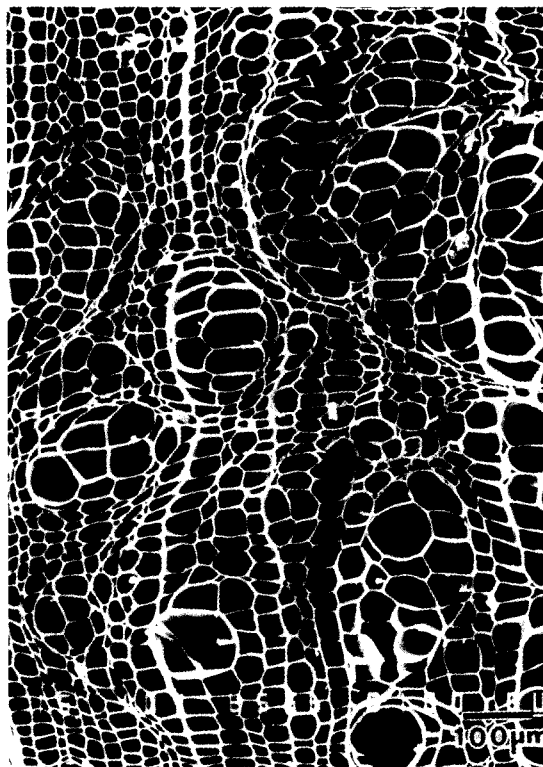


FIG. 2. Micrograph of secondary electron image on a transverse section of carbonized sugi sapwood specimen burned at 800°C with a raising rate of 115°C/min, showing an abnormal shrinkage and deformation of the cellular structure.

weight losses of 41–46% for colloidal silica-treated specimens and 51–53% for water glass-treated specimens and volumetric shrinkages of 41–53%. The weight loss decreased with increasing WPG values in the specimens. WMC specimens revealed the considerable small values of weight loss compared with untreated wood specimens. This is due to the existence of non-carbon substance or silica ( $\text{SiO}_2$ ) in the specimens. There was no great difference in weight loss and volumetric shrinkage among the burning temperatures of 600 to 1300°C, which is the same trend as untreated wood specimens.

Water glass-treated specimens were not provided for carbonization at 1300°C because the WPG values were much smaller and the weight losses were larger than those in colloidal silica-treated specimens. Also, in water glass-treated

TABLE 1. Weight percent gain (WPG), weight loss (WL), and volumetric shrinkage (VS) of carbonized specimens at different burning temperatures (BTs).

Code	Treatments	BT (°C)	WPG (%)	WL (%)	VS (%)
A	Untreated	600	—	74.2	54.6
B	Colloidal silica-treated	600	60.0	42.6	41.3
C	Water glass-treated	600	35.0	51.2	42.5
D	Untreated	1000	—	76.2	63.2
E	Colloidal silica-treated	1000	66.5	46.1	53.3
F	Water glass-treated	1000	37.4	52.8	48.3
G	Untreated	1300	—	75.8	62.2
H	Colloidal silica-treated	1300	83.1	41.2	42.2
I	Colloidal silica-treated	1300	79.0	43.7	46.5
J	Colloidal silica-treated	1300	77.0	44.1	48.9

Note: Holding times at target temperature: A-H 30 min, I 60 min, and J 120 min.

specimens burned at 600°C and 1000°C, granular silica was deposited mostly in the cell lumina, and silica with a crystal form was only occasionally observed with EPMA as described later.

#### X-ray diffraction

The results of X-ray diffraction are shown in Fig. 3 and Fig. 4. In X-ray diffraction patterns of carbonized untreated wood (charcoal) specimens (Fig. 3), the peak at  $2\theta = 22.5^\circ$  became broader

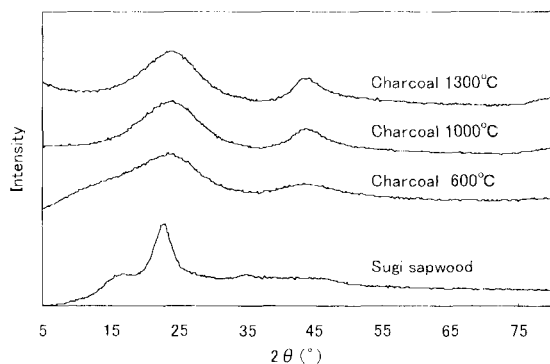


FIG. 3. X-ray diffraction patterns (CuK $\alpha$ ) of carbonized untreated wood (charcoal) specimens at burning temperatures of 600°C, 1000°C, and 1300°C for holding time of 30 min as well as untreated wood (sugi sapwood) specimens.

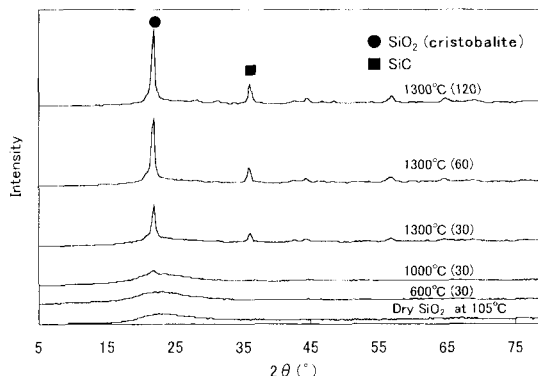
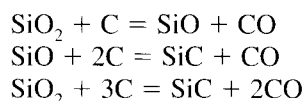


FIG. 4. X-ray diffraction patterns (CuK $\alpha$ ) of carbonized WMC specimens (colloidal silica-treated) at burning temperatures of 600°C, 1000°C, and 1300°C as well as SiO<sub>2</sub> dried at 105°C. Note: Figures in the parentheses show the holding time (minutes).

at burning temperature of 600°C compared with untreated wood specimens and remained almost unaltered even when the temperature increased up to 1300°C.

In contrast to charcoal, an interesting X-ray diffraction pattern was observed in carbonized WMC specimens (colloidal silica-treated) as shown in Fig. 4. The peak around  $2\theta = 20^\circ$  became much broader at 600°C, which was almost the same peak as in dry silica with an amorphous structure, and the small peak at  $2\theta = 22^\circ$  was just recognized at 1000°C. Furthermore, the peak  $2\theta = 22^\circ$  became distinctively sharp at 1300°C. This peak definitely reveals the change of crystalline structure of SiO<sub>2</sub>, that is, from the amorphous state to cristobalite (Borg and Smith 1969). In addition, it was found that the occurrence of the peak at  $2\theta = 35^\circ$  appeared first at 1300°C and tended to become greater with an increase in holding time. This peak definitely showed the formation of silicon carbide (SiC) in the carbonized WMC specimen. Ota and others (1997) reported that, in beech wood, SiC was formed above 1400°C after the treatment of tetraethyl orthosilicate infiltration and hydrolysis. This type of silicon carbide can be considered to be  $\beta$ -SiC (Ota et al. 1998; Greil et al. 1998a). The probable formation of SiC by reaction of carbon with silica

was proposed as the following formulae (Ota et al. 1995b):



From these experimental results, the formation of SiC proved to be directly related to the burning temperature. Carbonization at various temperatures of more than 1300°C and carbonization for longer holding times as well as in the atmosphere of other gas such as argon are in the next logical step to abundantly form SiC.

#### *Observation with EPMA*

Figure 5 shows secondary electron images on transverse sections of carbonized untreated wood (charcoal) specimens at different burning temperatures. The cellular structure of charcoal was almost similar to the original anatomy of Japanese cedar. The shape of tracheids in both earlywood and latewood was slightly deformed by carbonization. Abnormal deformation or shrinkage as shown in Fig. 2 was not observed in this experiment. Also, there was little difference in microstructure of charcoal among the burning temperatures of 600 to 1300°C.

Figure 6 shows EPMA micrographs of secondary electron images and X-ray maps of silicon taken in the same areas on transverse sections of carbonized WMC specimens impregnated with water glass at burning temperatures of 600°C and 1000°C. Aggregates of granular silica were observed abundantly in the lumina, and needle-like crystals of silica appeared less frequently. Also, the existence of silica in carbonized cell walls was detected from X-ray maps of silicon as already reported in WMC specimens using the water glass-boron compound system in spite of being very small in quantity in the cell walls compared with in the lumina (Furuno et al. 2001).

From X-ray maps of silicon (Fig. 7) for carbonized WMC specimens impregnated with colloidal silica at burning temperatures of 600°C and 1000°C, it was obvious that solid bodies ex-

isting in the cell lumina were silica, showing a homogeneous form in marked contrast to water glass-treated specimens. The shrinkage of these silica bodies filled in the cell lumina (Furuno et al. 2001) could be observed noticeably at both burning temperatures of 600°C and 1000°C, and there was a space between a silica body in each cell lumen and the cell wall. In addition, it was noted that silica was located in carbonized cell walls, as is carefully seen from X-ray maps of silicon, though the amount of silica in the cell walls was considered to be relatively less than that in the cell lumina (Furuno et al. 2001). For the carbonization at 1300°C (Fig. 8), silica bodies filled up the lumina in secondary electron images and the distribution of silicon in carbonized cell walls was also definitely observed in X-ray maps of silicon.

From both X-ray diffraction and EPMA observation, it was evident that the peak at  $2\theta \approx 35^\circ$  in X-ray diffraction pattern derived from the presence of silicon carbide (SiC) in the cell walls at burning temperature of 1300°C and the peak at  $2\theta = 22^\circ$  corresponded to silica existing in the cell lumina of which crystalline structure had been probably changed from amorphous silica to cristobalite. In conclusion, it is possible to produce SiC in the cell walls containing silica by carbonization at 1300°C in the atmosphere of inert gas such as nitrogen.

There is a need to investigate further the amount of silicon carbide formed in colloidal silica-treated specimens as well as the physical and mechanical properties of silica-silicon carbide composites such as density, strength, hardness, and others in the future.

#### CONCLUSIONS

From the results of X-ray diffraction, it was confirmed that silicon carbide (SiC) was formed by carbonizing wood-mineral composites impregnated with silica at 1300°C, and it was directly related to the burning temperature. From secondary electron images and X-ray maps of silicon, silica was located not only in the cell lumina as the crystalline structure of cristobalite

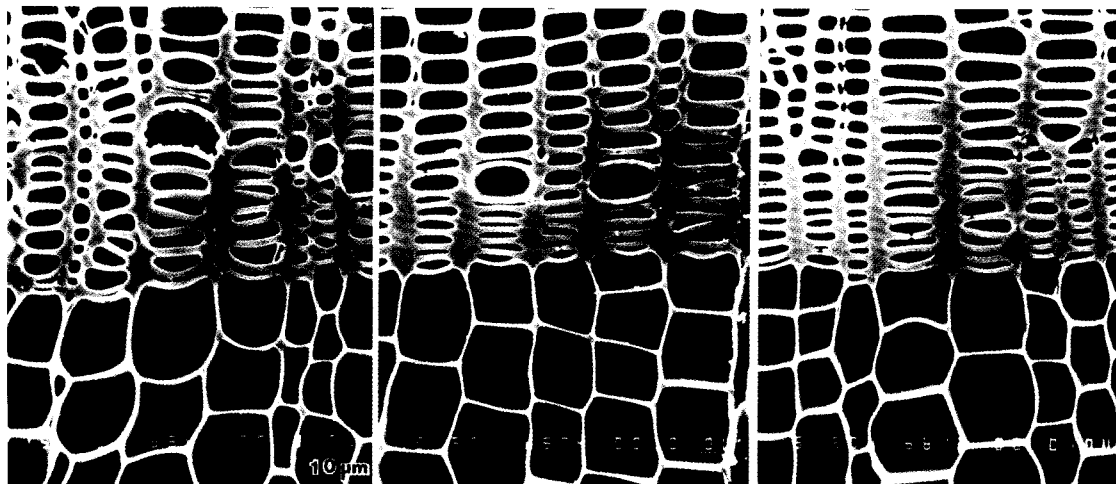


FIG. 5. Micrographs of secondary electron images on transverse sections of carbonized sugi sapwood specimens at burning temperatures of 600°C (left), 1000°C (center), and 1300°C (right).

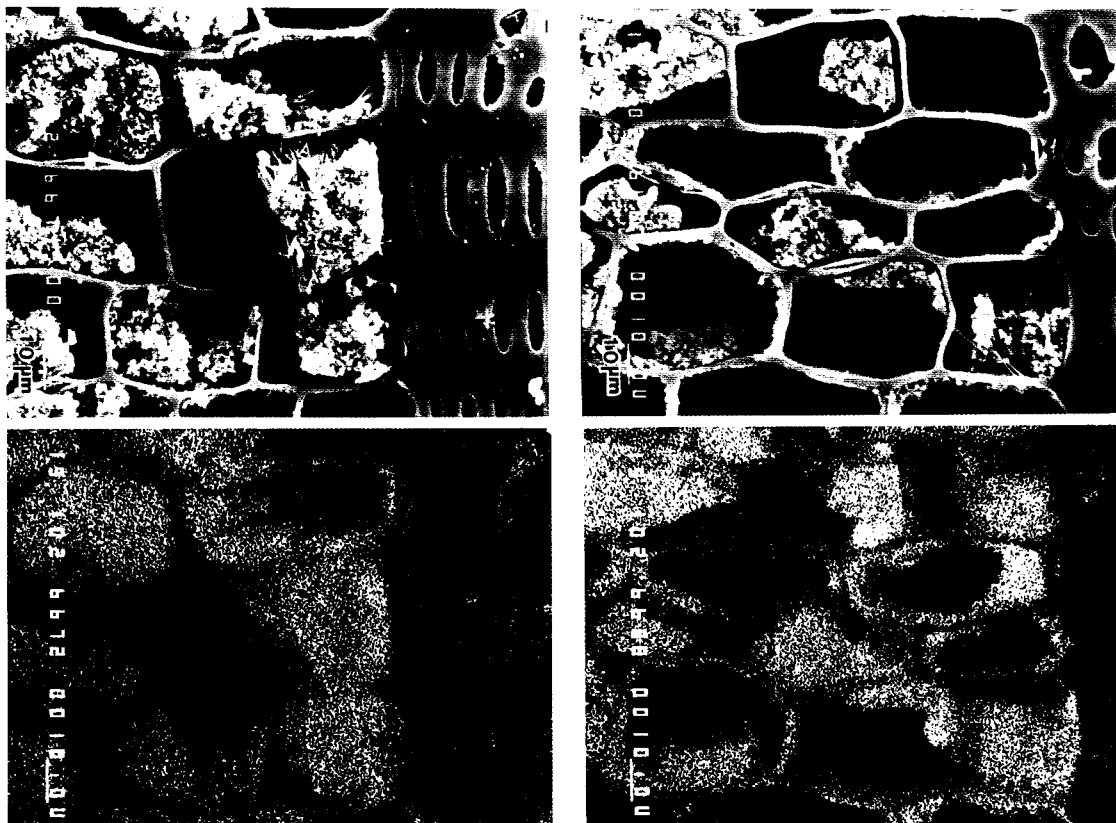


FIG. 6. EPMA micrographs of secondary electron images (upper) and Si- $K_{\alpha 1}$  X-ray maps (bottom) taken in the same areas on transverse sections of carbonized WMC specimens (water glass-treated) at burning temperatures of 600°C (left) and 1000°C (right). Arrows show needle-like crystals.

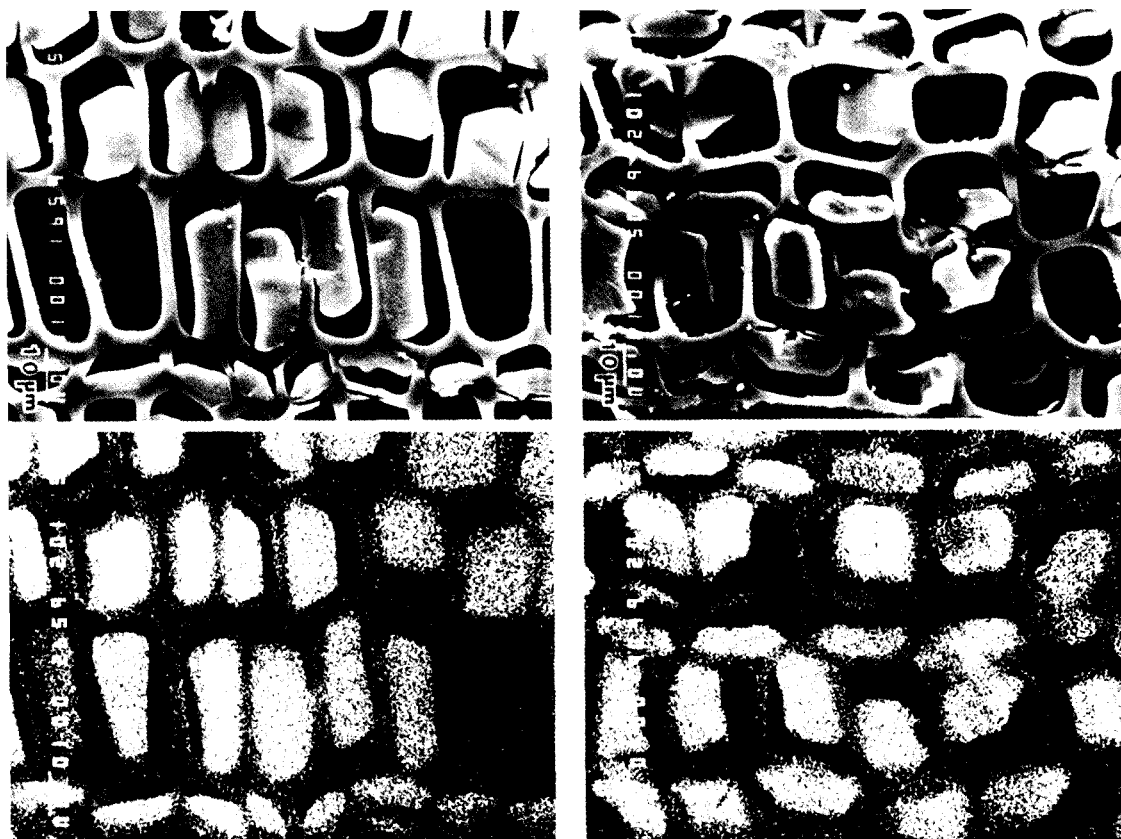


FIG. 7. EPMA micrographs of secondary electron images (upper) and Si-K $_{\alpha 1}$  X-ray maps (bottom) taken in the same areas on transverse sections of carbonized WMC specimens (colloidal silica-treated) at burning temperatures of 600°C (left) and 1000°C (right).

but also in the cell walls so that SiC was formed in the cell walls carbonized at 1300°C.

#### ACKNOWLEDGMENTS

The authors would like to thank Dr. Toshihiro Kitamura, Cooperative Research Center, Shimane University, and Mr. Eiji Udaka, Kagawa Prefectural Industrial Center, for their experimental assistance in carbonization and X-ray diffraction, respectively.

#### REFERENCES

- ABE, I. 1996. Production and application of charcoal absorbent. *Wood Industry* 51 (7):294–300.
- BORG, I. Y., AND D. K. SMITH. 1969. Calculated X-ray powder patterns for silicate minerals. The Geological Society of America, Inc., Boulder, CO. Pp. 747–749.
- BYRNE, C. E., AND D. C. NAGLE. 1997. Carbonization of wood for advanced materials applications. *Carbon* 35 (2):259–266.
- FURUNO, T., AND Y. IMAMURA. 1998. Combinations of wood and silicate Part 6. Biological resistances of wood-mineral composites using water glass-boron compound system. *Wood Sci. Technol.* 32 (3):161–170.
- , T. UEHARA, AND S. JODAI. 1993. Combinations of wood and silicate III. Some properties of wood-mineral composites using the water glass-boron compound system. *Mokuzai Gakkaishi* 39 (5):561–570.
- , R. TADOKORO, AND T. UEHARA. 1995. Glueability and fire resistance of wood-mineral composites using the water glass-boron compound system. *J. Soc. Mat. Sci., Japan* 44 (498):292–296.
- , S. AONO, AND T. UEHARA. 1996. Mechanical properties of wood-mineral composites using the water glass-boron compound system. *J. Soc. Mat. Sci., Japan* 45 (6):687–693.
- , T. KURIU, S. MATSUOKA, T. INOUE, AND T. UEHARA. 1997. Wood-mineral composites using colloidal

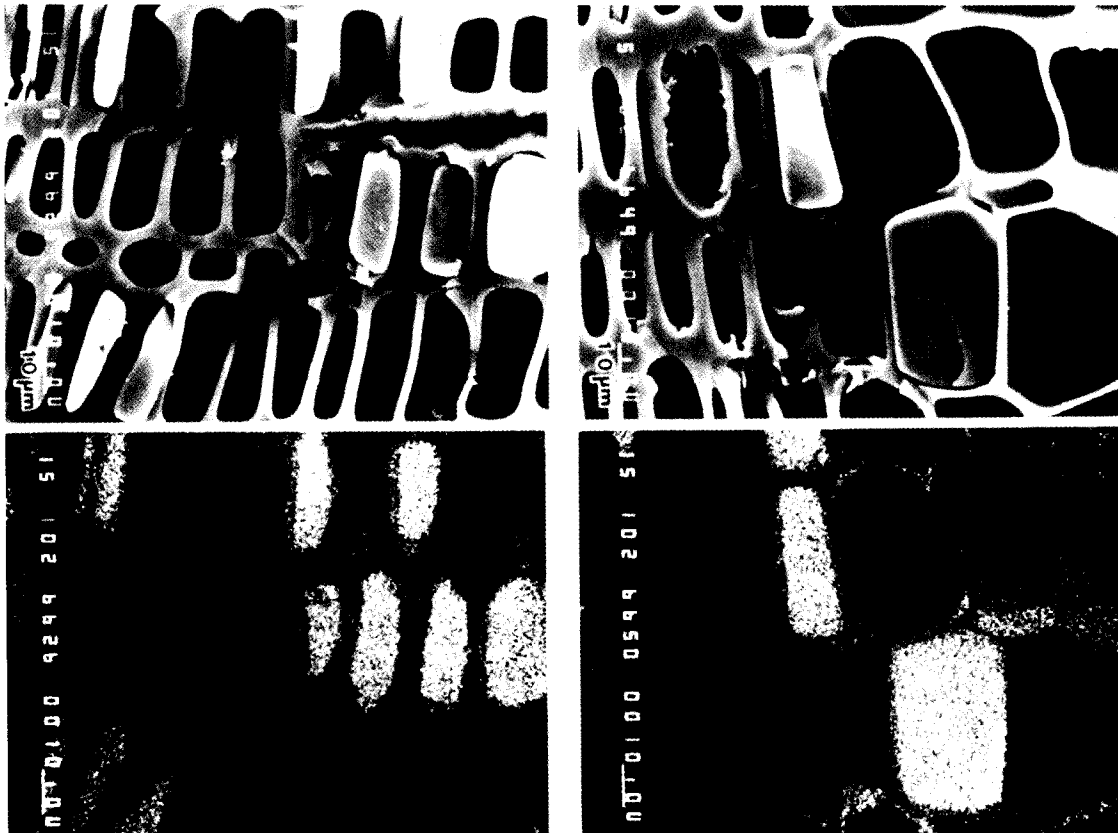


FIG. 8. EPMA micrographs of secondary electron images (upper) and Si-K $\alpha_1$  X-ray maps (bottom) taken in the same areas on transverse sections of carbonized WMC specimens (colloidal silica-treated) at burning temperature of 1300°C for holding time of 30 min (left) and 60 min (right).

- silica solution system and their properties. *J. Soc. Mat. Sci., Japan* 46 (4):401–407.
- , Y. IMAMURA, O. ASADA, AND S. KATOH. 1999. Some properties of wood-mineral composites using the colloidal silica solution system—Termite resistance, photo stability, hardness, and abrasion resistance. *J. Soc. Mat. Sci., Japan* 48 (3):245–250.
- , T. GOTO, AND S. KATOH. 2001. EPMA observation of wood-mineral composites using silicate-boron compound system and estimation of fire resistance by oxygen index method. *J. Mat. Sci., Japan* 50 (4):383–390.
- GREIL, P. 2001. Biomorphous ceramics from lignocelluloses. *J. Europ. Ceram. Soc.* 21:105–118.
- , T. LIFKA, AND A. KAINDL. 1998a. Biomorphous cellular silicon carbide ceramics from wood: I. Processing and microstructure. *J. Europ. Ceram. Soc.* 18:1961–1973.
- , ———, AND ———. 1998b. Biomorphous cellular silicon carbide ceramics from wood: II. Mechanical properties. *J. Europ. Ceram. Soc.* 18:1975–1983.
- ISHIHARA, S. 1997. Harmless conversion and removal of Nox by waste wood charcoal. *Eco Industry* 2 (2):15–20.
- KITAMURA, T., AND H. KATAYAMA. 2001. The effect of carbonizing conditions on the specific area of charcoal from sugi (*Cryptomeria japonica*) wood. *Mokuzai Gakkaishi* 47 (2):164–170.
- , S. MATSUMOTO, AND H. KATAYAMA. 1999. The effect of carbonizing conditions on the properties of charcoal absorbent from *Cryptomeria*. *Mokuzai Gakkaishi* 45 (2):171–177.
- , G. TAGUCHI, AND H. KATAYAMA. 2002. The effects of carbonizing conditions on the specific area of charcoal from sugi (*Cryptomeria japonica*) wood II. Effects of carbonizing temperature and carbon dioxide concentration in carbonizing atmospheres. *Mokuzai Gakkaishi* 48 (4):272–279.
- MARTÍNEZ-FERNÁNDEZ, J., F. M. VALERA-FERIA, AND M. SINGH. 2000. High temperature compressive mechanical behavior of biomorphous silicon carbide ceramics. *Scripta Mater.* 43 (9):813–818.



- OYA, T., M. TAKAHASHI, T. HIBI, M. OZAWA, S. SUZUKI, AND Y. HIKICHI. 1995a. Biomimetic process for producing SiC "wood." *J. Am. Ceram.* 78 (12):3409–3411.
- , Y. HIKICHI, AND T. HIBI. 1995b. SiC ceramic mimicking fossil wood. *Annual Report of the Ceramics Research Laboratory, Nagoya Institute of Technology* 5:33–39.
- , H. ICHYAMA, Y. HIKICHI, AND H. AKAHANE. 1997. Production of ceramic wood by mimicking fossil wood. *Annual Report of the Ceramics Research Laboratory, Nagoya Institute of Technology* 7:21–24.
- , Y. HIKICHI, H. KAWAKAMI, AND H. AKAHANE. 1998. Preparation of SiC ceramic woods by mimicking fossil woods—No. 3. *Annual Report of the Ceramics Research Laboratory, Nagoya Institute of Technology* 8:39–47.
- YATAGAI, M. 1997. Charcoal—Characterization and utilization. *Wood Industry* 52 (10):472–477.