The Changes in Microstructure and Thermal Constant in Conversion of Carbonized Wood to Silicon Carbide Composite

Joko Sulistyo, Toshimitsu Hata, and Sri Nugroho Marsoem

Abstract

Carbonized wood which possesses microstructure with random orientation graphitic crystallites and with pores between the graphitic crystallites, is potentially developed into new material of silicon carbide (SiC) composite, a high performance material for engineering purposes. This paper investigates the development of the microstructure in the turbostratic carbon phase and the formation of SiC crystal from the reaction of carbon and SiO_2. Results show the turbostratic microstructure in carbonized wood lead to the possible formation of SiC compound in the manufacturing of $SiC/SiO_2/C$ composite. The heat treatment at 1800ºC on the mixture of SO_2 and carbonized wood creates the formation of SiC compound, which improves the degree of microstructure ordering. The improvement of microstructure turbostratic carbon and the growth of graphitic crystallites in turbostratic carbon improves the thermal conductivity of $SiC/SiO_2/C$ composite comparing with those of carbonized wood composite.

Keywords : carbonized wood; $SiC/SiO_2/C$ composite; microstructure; thermal conductivity.

Introduction

Recently, considerable interest has developed in the use of wood-based carbon material as a new source of carbon for engineering applications (Byrne and Nagle 1997). It represents the carbon-neutral approach based on the renewable resources such as wood as precursor to deliver the new function of carbon material demands in the modern sustainable society (White 2015). Currently, carbonized wood is used for heavy metals adsorber (Pulido et al. 2001), electric magnetic shielding (Wang and Hung 2002), fire retardant wood composites (Subyakto et al. 2004), thermo-electric material (Fujisawa et al. 2004), electrical and thermal conductors (Sulistyo et al. 2009; 2010), carbide ceramics (Greil 2001), and in situ formation of nano materials (Hata et al. 2005; Sulistyo et al. 2012). These various applications of carbonized wood-based materials refers to the pores and microstructure in carbonized wood. Then, the exploiting pores and microstructure in the carbonized wood may lead to the new applications of material.

Theoretically, carbonized wood consists of porous carbon with turbostratic microstructure in which graphitic carbon crystallites have a disordered arrangement with pores as gaps between the graphitic crystallites (Rodriguez-Reinoso and Molina-Sabio 1992). The pores possess an interconnected network in the interior of solid matrix of carbonized wood (White 2015). The microstructure and pores in carbonized wood are determined by the heat treatment conditions, including temperature, reaction time and heating rate. The heat treatment in between 300~1400ºC causes carbon crystallites to grow and increases the ordering in the microstructure of the carbonized biomass (Paris et al. 2005). Incorporating more carbon atoms into turbostratic crystallites to form large

graphene sheets increases the electric conductivity phase in the carbonized wood (Xie et al. 2008). The thermal conductivity of carbonized wood is about 0.9 W/mK (Parfeneva et al. 2006).

Porosity and turbostratic structure in the carbonized wood are preserved at high temperatures which creates the possibility of engineering lignocellulosic ceramics manufacturing such as silicon carbide (SiC). In previous study, a simple method was developed to convert carbonized wood into SiC composite (Sulistyo et al. 2010) with a wide range of electrical and thermal conductivities. The conversion of carbonized wood into SiC involves infiltration through the porosity in carbonized wood and was then followed by reaction between carbon element with Si or gaseous phase of SiO or liquid phase of SiO_2. Carbonized wood serves as a host for a fluid or gas medium, which reacts with carbon to form a carbide phase (Greil 2001). After Si melt infiltration, the stepwise reaction of silicon and carbon results in the simultaneous formation of a nano-graine SiC layer and a coarsed-grained SiC phase on the inner pore surfaces (Zollfrank and Sieber 2005). However, the development of turbostratic microstructure in the residual carbonized wood during the heat treatment and conversion of the carbonized wood into SiC crystal remains indistinct. This paper investigates both the development of microstructure in residual carbonized wood and the formation of SiC in the microstructure of carbonized wood. The effect of heat treatment on the microstructure development and the morphology of carbonized wood and the formation of silicon carbide compunds in the microstructure carbonized wood were observed by Raman spectroscopy, scanning electron microscope (SEM) and transmission electron microscope (TEM). The thermal constants were measured by a laser flash method.

Materials and Methods

Carbonized wood were obtained by heating sugi wood (*Cryptomeria japonica* D.Don) particles at a heating rate of 4ºC/min and were then maintained at constant temperature of 700ºC for an hour in an Argon gas with flowing rate of 100 mL/min in a laboratory scale electric furnace. Carbonized wood particles were then granulated using a vibration mill and sieved with wire mesh screens of 63 and 90 μm apertures to obtain range of 63~90 μm. Figure 1 shows the SEM image of a particle of carbonized wood exhibiting the cellular structure of wood material.

A dry weight of 0.08 g of carbonized wood powder in a graphite die with a diameter 10 mm was then heated to 700ºC at a rate of 71ºC/min with a holding time of 15 min under vacuum conditions using a pulse current sintering apparatus (VCSP-II, SS Alloy, Hiroshima). A pressure of 50 MPa was applied from the start of the heating and it was released immediately after the reaction. It is expected this heat treatment condition was not altered the microstructure of carbonized wood. This heat treatment obtained a 10 mm diameter of carbonized wood composite samples.

Some of the carbonized wood was submerged in the silica solution containing 15% SiO_2 concentration in ethyl alcohol and it was held under vacuum condition of 1 kPa for 90 min. The carbonized wood infiltrated with SiO_2 was kept at room temperature until it dried. A dried weight of 1 g material was then placed in the graphite die and was then heated to 1800ºC at a rate of 250ºC/min with a holding time of 30 min under 15 MPa pressure and N_2 gas flow of 1 L/min using a pulse current apparatus. The 5-mm-thickness silicon carbide composite samples obtained were cut into discs with a thickness of approximately 0.8 mm. This sample similar with those published by Sulistyo *et al.* (2010) (denoted as $SiC/SiO_2/C$ composite).
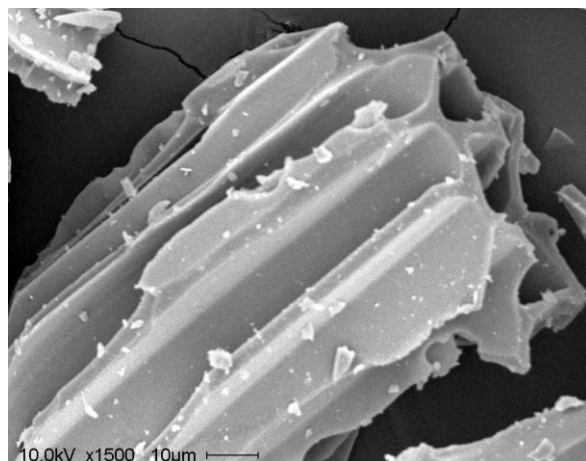

Figure 1. SEM image of a particle of carbonized wood that exhibits the cellular structure as in the original wood.
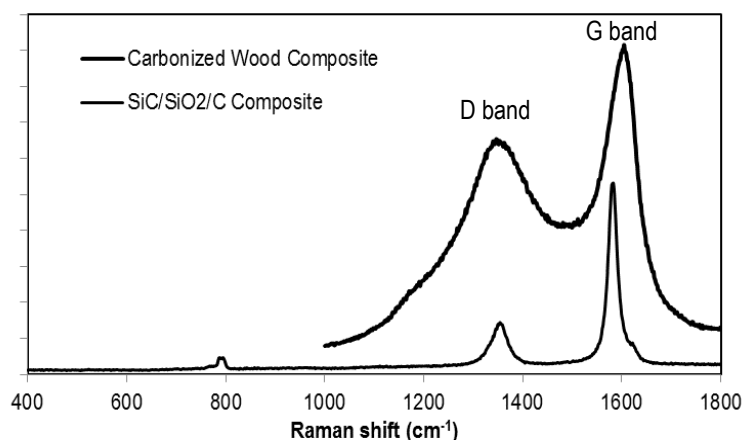

Figure 2. Raman spectra in the range of 400-1800 cm^{-1} of carbonized wood composite and $SiC/SiO_2/C$ composite. *TO* transver optic, *D band* disorder, *G band* graphite

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Table 1. Raman parameters of carbonized wood composite and SiC/SiO$_2$/C composite.

	Position (cm^{-1})			G FWHM (cm^{-1})	D FWHM (cm^{-1})	I_D/I_G	L_a (Å)
	TO	G band	D band				
Carbonized wood composite		1601	1346	63.3	112.9	0.5612	77.5
SiC/C Composite	791	1583	1354	21.8	36.0	0.2686	161.9

The morphology of composites was observed in scanning electron microscopy (SEM, JEOL-JSM-5310). The samples were then observed directly without any coating. Transmission electron microscopy (TEM, JEOL-JEM-2100F), equipped with electron energy-loss spectroscopy (EELS, GATAN) was performed to observe chemical composition on a silicon carbide (SiC/SiO$_2$/C) composite. Thin samples for TEM were prepared by a SEM–FIB (JEOL-JIB4500). Tungsten was used to protect the surface of the sample, and a 30 kV Ga ion beam was used in the preparation of the thin sample.

A Raman spectroscope (Renishaw inVia, England) equipped with an air-cooled CCD detector was used to analyze the microstructure of carbonized wood and silicon carbide composites. An argon laser (514.5 nm) was adopted as an excitation source. Spectra were measured in the 400~1,800 cm^{-1} range. Six 30-s and seven 10-2 accumulations gave adequate signal-to-noise ratio of the spectra of carbonized wood composite and SiC/SiO$_2$/C composite, respectively. The wave number was calibrated using the 520 cm^{-1} line of a silicon wafer. Spectral processing was performed using WiRE 2 software. The graphitic crystallite size or coherence length (L_a) was determined by Tuinstra and Koenig's formula (1970) as mentioned below:

$$L_a = \frac{(43.5 \text{ Å})}{I_D/I_C} \tag{1}$$

The thermal diffusivity (α) and the specific heat (C_p) were measured from room temperature to 150°C in air condition. by the laser flash method using a thermal constant analyzer (Ulvac, TC-7000H). The thermal diffusivity was calculated as follows:

$$\alpha = \frac{0.1388 \, d^2}{t_{1/2}} \tag{2}$$

where d is the thickness of the specimen and $t_{1/2}$ is the time required for the temperature of the rear face to increase to one-half of the maximum temperature. The specific heat capacity was calculated as

$$C_p = \frac{Q}{d \, \rho \, \Delta T_0} \tag{3}$$

where Q is the absorbed quantity of heat, d is the thickness of test piece, ρ is the density of the test piece, and ΔT_0 is the extrapolated temperature increase. The thermal conductivity (K_T) was calculated by the following equation:

$$K_T = \rho \, C_p \, \alpha \tag{4}$$

where ρ is the bulk density of the specimen (g/cm^3), C_p is specific heat (J/g/K), and α is the thermal diffusivity (m^2/s).

Results and Discussion

Figure 2 shows Raman spectra in the 400~1800 cm^{-1} region of carbonized wood and silicon carbide composite. Both curves exhibited G and D bands at around 1583~1601 and 1346~1354 cm^{-1} which correspond to the presence of graphitic order and a structural disorder respectively (Tuinstra and Koenig 1970). D band is associated with turbostratic carbon since it is absent in perfect graphite (Paris et al. 2005). The full width of half maximum (FWHM) of both G and D bands of silicon carbide composite was much narrower than those of carbonized wood composite as shown in Figure 2 and Table 1. The narrowing of G and D bands correspond an improvement of degree of ordering in the carbon microstructure of silicon carbide (SiC/SiO$_2$/C) composite after heat treatment at 1800°C. The heat treatment at 1800°C also caused the growth of graphitic crystallites as shown the L_a value of graphitic crystallite in carbonized wood composite is about 77.5 Å, which was smaller than that of 161.9 Å in silicon carbide composite. During the heat treatment, the low density disorder carbon incorporated into the larger graphene sheet of turbostratic carbon to allow the uniform growth graphitic crystallites (Kercher and Nagle 2003). The reaction of SiO$_2$ and carbonized wood forms SiC in silicon carbide (SiC/SiO$_2$/C) composite. It was confirmed with a single peak at 791 cm^{-1} corresponding to the transverse optic (TO) phonon mode of cubic ß-SiC (Ward et al. 2004). The Raman spectra showed that after the heat treatment at 1800°C on the infiltrated SiO$_2$ carbonized wood caused the formation of SiC crystal, the improvement of degree of ordering in turbostratic microstructure carbon and the growth of graphitic crystallites of turbostratic carbon. Previous study showed that this sample also consisted of residual SiO$_2$ compound besides of SiC and turbostratic carbon (Sulistyo et al. 2010). Therefore, this sample is denoted as SiC/SiO$_2$/C composite in this study.

Figure 3a shows a SEM image of the cross section of carbonized wood composite. The SEM image shows the particles in carbonized wood composite maintained the cellular structure as in the original wood. The heat treatment at 700°C under a pressure of 50 MPa influenced by closely packed the particles but without any changes in the cellular structure of particles which were similar with that of carbonized wood particle as shown in Figure 1. The higher magnification of the square area shows the carbonized wood particles exhibiting smooth surfaces. There were cracks found on the particle due to the high pressure during the heat treatment as shown by an arrow in Figure 3b.
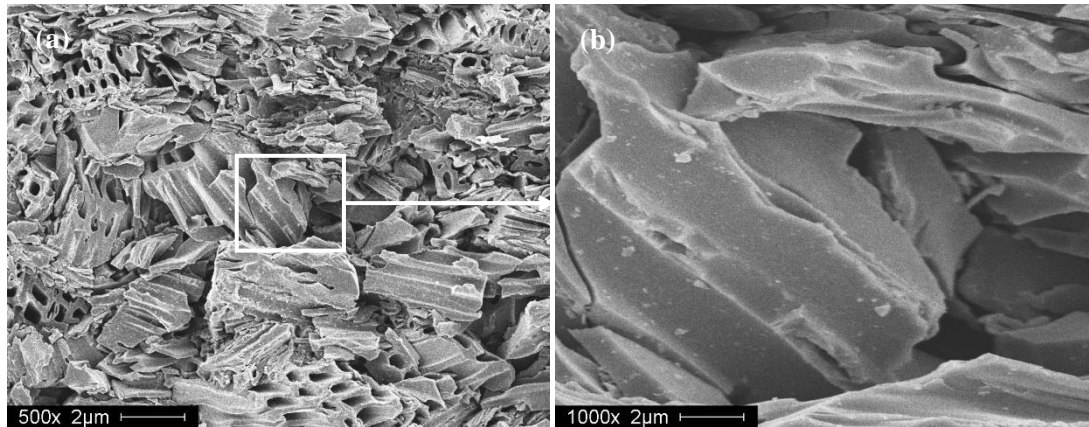
Figure 3. SEM images of (a) carbonized wood composite and (b) the higher magnification of the square area in the left image. *SEM* scanning electron microscopy.

Figure 4a shows a SEM image of the cross section of silicon carbide ($SiC/SiO_2/C$) composite. The morphology of carbonized wood particle infiltrated SiO_2 after sintering at 1800ºC which was different with that of carbonized wood composite as shown in Figure 3. The higher magnification of the square area shows rough surfaces on the cracked particles in the sample. The rough surfaces on particles indicated the formation of SiC from the reaction of SiO_2 with carbonized wood. The solid phase of SiO_2 layer in the surface of carbonized wood particles melted and then it reacted with carbonized wood in the interface area. The formation of SiC has been discussed in previous paper (Sulistyo *et al*. 2010). The turbostratic microstructure in carbonized wood with pores which are voids between graphitic crystallite (Rodriguez-Reinoso and Molida-Sabio 1992) causes the possibility of infiltration of melted SiO_2 into the interior part of carbonized wood and reacts with carbon elements in the surface of graphene sheet to form silicon carbide (SiC). The SEM observation shows a good correlation with the Raman spectroscopy results.
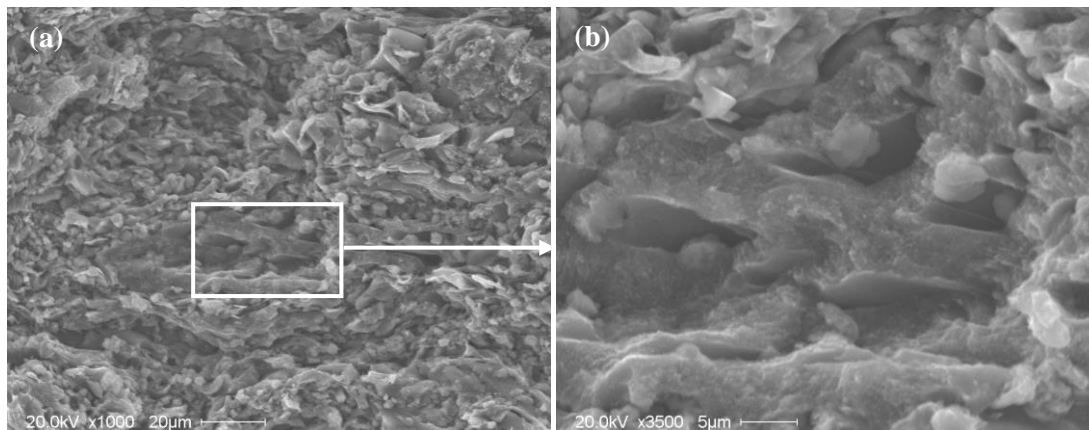

Figure 4. SEM images of (a) $SiC/SiO_2/C$ composite and (b) the higher magnification of the square area in the left image. *SEM* scanning electron microscope

TEM-EDS analysis was implemented to examine the chemical compositions of silicon carbide ($SiC/SiO_2/C$) composite after the heat treatment at 1800ºC. The EDS spectra are shown in Figure 5, which shows that $SiC/SiO_2/C$ composite contained of C corresponds to the turbostratic carbon on the inner part; Si and C corresponds to SiC layer on the outer part of samples. The TEM-EDS analysis confirmed that $SiC/SiO_2/C$ composite consist of turbostratic carbon in the interior part and SiC layer on the surface of the composite.

Figure 6 illustrates the schematic microstructure of turbostratic carbon in which graphitic crystallites are randomly arranged and pores occurring as voids between the graphitic crystallites. The graphitic crystallites show a limited diameter size (L_a). The disorder structure of carbonized wood possessing pores inside the

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microstructure provides the possibility infiltration of SiO_2 into the interior part of carbon during the heat treatment at 1800 ºC. The melted SiO_2 reacts with carbon elements in the surface of graphitic crystallites to form SiC during the heat treatment. During the heat treatment graphitic crystallites are also grown because of the incorporation of disorder carbon into graphene sheets to create larger diameter size (L_a). The heat treatment at high temperature of carbonized wood infiltrated SiO_2 brings an improvement of the degree of ordering the carbon microstructure in SiC/C composite.
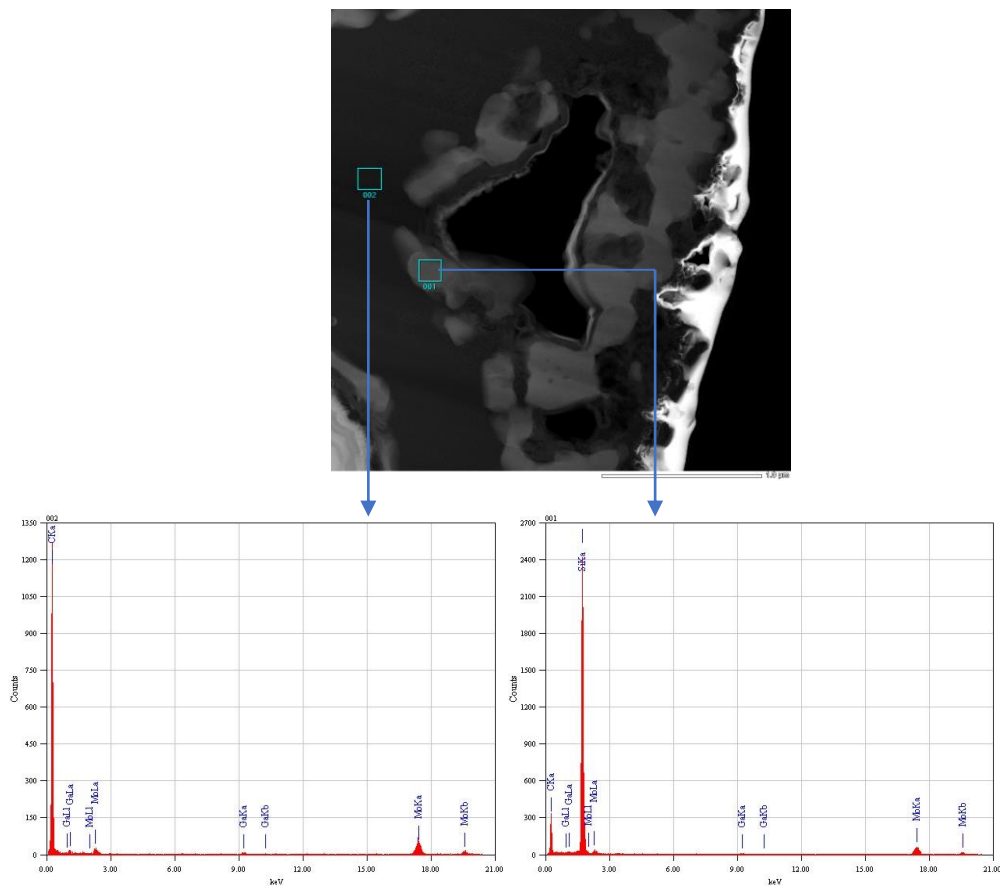

Figure 5. TEM-EDS spectra of SiC/SiO$_2$/C taken at turbostratic carbon phase (left) and SiC phase (right). *TEM* transmission electron microcope; *EDS* energy dispersive spectroscopy

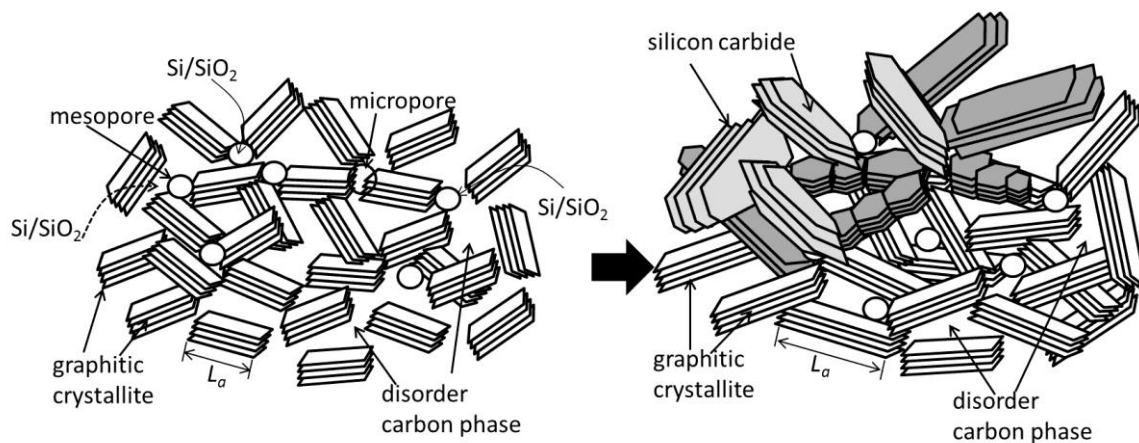Figure 6. Schematic of the microstructure in carbonized wood and that after conversion to SiC/SiO$_2$/C composite after heat treatment at 1800ºC.

Figure 7 shows the thermal dependence of thermal conductivity of carbonized wood and SiC/SiO$_2$/C composites. The thermal conductivity of carbonized wood composite and of SiC/SiO$_2$/C composite demonstrated large difference characteristics in temperature dependence, even both materials transport heat primarily by phonons (Fujisawa *et al.* 2005). The thermal conductivity of carbonized wood composite increased with the increase of measuring temperature, in the contrary that of SiC/SiO$_2$/C composite that shows decreasing trend. Temperature dependence of thermal conductivity of SiC/SiO$_2$/C composite was similar with SiC/C composite in previous study (Liu and Lin 1996; Fujisawa *et al.* 2005). Therefore microstructural change as shown in SEM, Raman's spectroscopy and TEM-EDS analyses influence the thermal conductivity. The thermal conductivity of carbonized wood composite was much improved after the heat treatment, at 1800ºC that was determined by the improvement of degree of order in the microstructure and the growth of graphitic crystallites in carbonized wood phase (Chung 2002; Xie *et al.* 2008) and also the formation of SiC crystal which is possessing a high thermal conductivity (Zhou *et al.* 2004) in SiC/SiO$_2$/C composite.
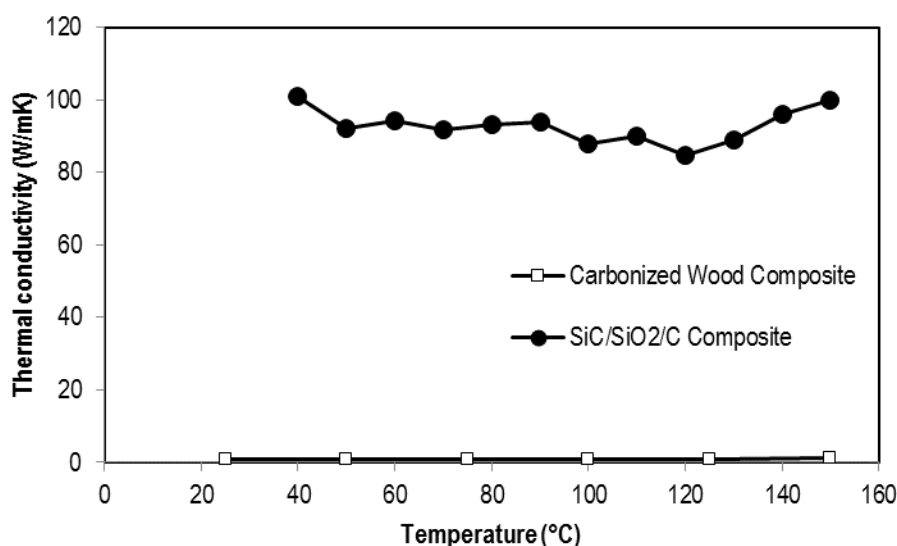

Figure 7. Thermal conductivity of carbonized wood composite and SiC/SiO$_2$/C composite as a function of temperature in range of 25~150 ºC.

Conclusions

The turbostratic microstructure in carbonized wood caused the possibility of the formation of SiC crystal in the manufacturing of SiC/SiO$_2$/C composite from carbonized wood in the heat treatment of 1800ºC. The heat treatment at 1800ºC on the mixes of SO$_2$ and carbonized wood caused by the formation of SiC compound, the improvement of degree of ordering in turbostratic microstructure carbon and the growth of graphitic crystallites of turbostratic carbon which improved the thermal conductivity of SiC/SiO$_2$/C composite compared with those of carbonized wood composite.

References

Chung, D.D.L. 2002 Review Graphite. Journal of Materials Science 37: 1475-1489.

Byrne, C.E.; D.C. Nagle. 1997. Carbonization of Wood for Advanced Materials Applications. Carbon 35:259-266.

Fujisawa, M.; T. Hata; P. Bronsveld; V. Castro; F. Tanaka; H. Kikuchi; T. Furuno; Y. Imamura. 2004. SiC/C Composites Prepared from Wood-Based Carbons by Pulse Current Sintering with SiO$_2$: Electrical and Thermal Properties. Journal of European Ceramic Society 24: 3575-3580.

Fujisawa, M.; T. Hata; P. Bronsveld; V. Castro; F. Tanaka; H. Kikuchi; Y. Imamura. 2005. Thermoelectric Properties of SiC/C Composites from Wood Charcoal by Pulse Current Sintering. Journal of European Ceramic Society 25: 2735-2738.

Greil, P. 2001. Biomorphous Ceramics from Lignocellulosic, Journal of European Ceramic Society 21: 105-118.

Hata, T.; V. Castro; M. Fujisawa; Y. Imamura; S. Bonnamy; P. Bronsveld; H. Kikuchi. 2005. Formation of Silicon

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Carbide Nanorods from Wood Based Carbons. Fuller., Nanotub. and Carbon Nanostruct. 13: 107-113.

Kercher, A.K.; D.C. Nagle. 2003. Microstructural Evolution during Charcoal Carbonization by X-Ray Diffraction Analysis. Carbon 41: 15-27.

Liu, D.M.; B.W. Lin. 1996. Thermal Conductivity in Hot-Pressed Silicon Carbide. Ceramics International 22: 407-411.

Paris O.; C. Zollfrank; G.A. Zickler. 2005. Decomposition and Carbonization of Wood Biopolymers-A Microstructural Study of Softwood Pyrolysis. Carbon 43: 53-66.

Parfeneva, L.S.; T.S. Orlova; N.F. Kartenko; N.V. Sharenkova; B.I. Smirnov; I.A. Smirnov; H. Misiorek; A. Jezowski; J. Mucha; A.R. de Arellano-Lopez; J. Martinez-Fernandez; F.M. Varela-Feria. 2006. Thermal and Electrical Properties of a White-eucalyptus Carbon Preform for SiC/Si Ecoceramics. Phys. Sol. State 48: 441-446.

Rodriguez-Reinoso, F.; M. Molina-Sabio. 1992. Activated Carbon from Lignocellulosic Materials by Chemical and/or Physical Activation: An Overview. Carbon 30: 1111-1118.

Subyakto; T. Hata; I. Ide; T. Yamane; S. Kawai. 2004. Fire Protection of a Laminated Veneer Lumber Joint by Wood Carbon Phenolic Spheres Sheeting, Journal of Wood Science 50: 157-161.

Sulistyo, J.; T. Hata; M. Fujisawa; K. Hashimoto; Y. Imamura; T. Kawasaki. 2009. Anisotropic Thermal Conductivity of Three-layer Laminated Carbon-graphite Composites from Carbonized wood. Journal of Materials Science (44): 734-744.

Sulistyo, J.; T. Hata ; H. Kitagawa; P. Bronsveld; M. Fujisawa; K. Hashimoto; Y. Imamura. 2010. Electrical and Thermal Properties with Different Morphology from Carbonized Wood. J. Materials Science 45: 1107-1116.

Sulistyo, J.; T. Hata; S.N. Marsoem. 2012. Formation of SiC Rods in Composites of SiC/SiO2/C from Carbonized Wood Infiltrated with Ethylsilicate-40. Wood Research Journal 2(1): 34-41.

Tuinstra, J.; J.L. Koening. 1970. Raman Spectrum of Graphite. The Journal of Chemical Physics 53: 1126-1130.

Pulido, L.L.; T. Hata; Y. Imamura; S. Ishihara; T. Kajimoto. 1998. Removal of Mercury and Other Metals by Carbonized Wood Powder from Aqueous Solution of Their Salts, J. Wood Sci. 44: 237-243.

Wang, S.Y.; C.P. Hung. 2003. Electromagnetic Shielding Efficiency of the Electric Field of Charcoal from Six Wood Species, J. Wood Sci. 49: 450-454.

Ward, Y.; R.J. Young; R.A. Shatwell. 2004. Application of Raman Spectroscopy to the Analysis of Silicon Carbide Monofilaments. Journal of Materials Science 39: 6781-6790.

White, R.J. 2015. The Search for Functional Porous Carbons from Sustainable Precursors. In Porous Carbon Materials from Sustainable Precursors, Chapt. 1. Ed. R.J. White. RSC Green Chemistry No. 32. The Royal of Chemistry. Cambridge. UK.

Xie, X.; B. Goodell; Y. Qian; M. Peterson; J. Jellison. 2008. Significance of the Heating Rate on the Physical Properties of Carbonized Maple Wood. Holzforschung 62: 591-596.

Zhou, Y.; K. Hirao; K. Watari; Y. Yamauchi; S. Kanzaki. 2004. Thermal Conductivity of Silicon Carbide Densified with Rare-earth Oxide Additives. Journal of the European Ceramic Society 24): 265-270.

Zollfrank, C.; H. Sieber. 2005. Microstructure Evolution and Reaction Mechanism of Biomorphous SiSiC Ceramics. Journal of American Ceramic Society 88: 51-58.

Joko Sulistyo and Sri Nugroho Marsoem
Faculty of Forestry, Universitas Gadjah Mada, INDONESIA
Jl. Agro No. 1. Bulaksumur, Yogyakarta, Indonesia 55281
Tel   : 62-274-6491428
Fax   : 62-274-550541
E-mail   : jsulistyo@ugm.ac.id

Toshimitsu Hata
Laboratory of Innovative Humano-habitability
Research Institute for Sustainable Humanosphere,
Kyoto University
Uji Campus, Gokasho, Uji, Kyoto 611-0011, JAPAN.
Tel.   : +81-774-38-3601
Fax.   : +81-774-38-3600
E-mail   : hata@rish.kyoto-u.ac.jp