

## Effect of Specific Surface Area on the Reaction of Silicon Monoxide with Porous Carbon Fiber Composites

Min Jin Park and Jae Chun Lee

Department of Inorganic Materials Engineering, Myongji University,  
San 38-2, Namdong, Youngin, Kyunggi-do, Korea  
(Received July 16, 1998)

Porous carbon fiber composites (CFCs) having variable specific surface area ranging 35~1150 m<sup>2</sup>/g were reacted to produce silicon carbide fiber composites with SiO vapor generated from a mixture of Si and SiO<sub>2</sub> at 1673 K for 2 h under vacuum. Part of SiO vapor generated during conversion process condensed on to the converted fiber surface as amorphous silica. Chemical analysis of the converted CFCs resulting from reaction showed that the products contained 27~90% silicon carbide, 7~18% amorphous silica and 3~63% unreacted carbon, and the composition depended on the specific surface area of CFCs. CFC of higher specific surface area yielded higher degree of conversion of carbon to silicon carbide and conversion products of lower mechanical strength due to occurrence of cracks in the converted carbon fiber. As the conversion of carbon to silicon carbide proceeded, pore size of converted CFCs increased as a result of growth of silicon carbide crystallites, which is also linked to the crack formation in the converted fiber.

**Key words:** Carbon fiber composites, Activated carbon fibers, Silicon carbide, Carbonization, Surface areas, Mechanical properties.

### I. Introduction

Gas-solid reactions between SiO vapor with various types of carbon have been studied to obtain silicon carbide materials as a catalyst support or for a structural use. Since Kennedy and North have prepared SiC powders by reacting carbon powders with SiO vapor generated from mixtures of Si and SiO<sub>2</sub> under vacuum,<sup>1</sup> much effort has been devoted to produce high specific surface area SiC powder<sup>2,6</sup> or high strength SiC fiber.<sup>6,7</sup> Ledoux *et al.* extended the work of Kennedy and North to produce silicon carbide powders of high specific surface area by reacting SiO vapor and activated carbon powders.<sup>3,4</sup> They concluded that a complete conversion of the active carbon into silicon carbide was difficult to obtain due to the effect of heat treatment on the active carbon structure which resulted in a decrease in the conversion rate.<sup>3</sup> Okada *et al.* investigated the reaction between activated carbon fiber and SiO vapor.<sup>6</sup> They claimed that complete reaction occurred at 1473 K and 1573 K in 10 h and 4 h, respectively. Ling and Rand studied the conversion process of high strength carbon fibers in the form of a plain 2D woven cloth to SiC at 1523~1573 K and found severe radial cracks in fully converted fibers.<sup>7</sup> In this paper, in a production of silicon carbide bonded silicon carbide fiber composites by reaction of carbon fiber composites (CFCs) with SiO vapor, the effect of specific surface area (SSA) of CFC at a constant reaction temperature has been investigated. It is the purpose of this paper to discuss the effect of SSA of CFC on the degree of conversion of carbon to SiC and various properties of converted CFCs.

### II. Experimental Procedure

#### 1. Raw materials and preparation of carbon fiber composites

As a carbon source to react with SiO vapor, monolithic carbon fiber composite (CFC) samples of various specific surface areas (SSA) ranging 35~1150 m<sup>2</sup>/g were prepared in this study. Disc shaped samples, 20 mm in diameter and 10 mm thick, were vacuum molded from a mixture of PAN based carbon fiber and phenolic resin particles. The weight ratio of phenolic resin to the carbon fiber was 3:7. After drying followed by carbonization of the samples at 1123 K in flowing N<sub>2</sub>, carbon bonded carbon fiber composites were obtained. The porosity and density of CFC measured by Archimedes principle were about 77% and 0.39 Mg/m<sup>3</sup>, respectively. CFC preforms of various SSA were prepared by CO activation at 1073 K for different periods. In this way four different groups of CFCs having SSA values, 35 m<sup>2</sup>/g, 497 m<sup>2</sup>/g, 692 m<sup>2</sup>/g and 1150 m<sup>2</sup>/g, were obtained and designated as 35-CFC, 497-CFC, 692-CFC and 1150-CFC, respectively. More detailed accounts of the preparations and properties of porous CFC are given elsewhere.<sup>8</sup>

#### 2. SiO/C reaction

It has been known that SiO vapor can be generated by reducing SiO<sub>2</sub> with elemental Si at elevated temperature.<sup>9</sup>



The reaction of silicon monoxide with carbon is described by the equation



From Eqs. (1) and (2), we can determine the amount of Si/SiO<sub>2</sub> relative to carbon for stoichiometric reaction. In the present study mass of the pellet was four times larger than the one necessary for the presumed stoichiometric reaction between CFC and SiO vapor.

The porous CFC samples were reacted with SiO vapor generated from a pelletized mixture of Si and SiO<sub>2</sub> powders at 1673 K for various hold times ranging 10 to 120 min. A graphite pot used as a sample holder containing both the CFC samples and the pellet was placed in a tubular alumina reactor (52 mm I.D and 900 mm long). A vacuum pressure of 13.3 Pa was maintained before SiO vapor generation. The graphite reaction pot (35 mm O.D and 8 mm long) has one annular shaped end cap that holds the ACFC sample. The end cap is threaded and can be screwed to allow the gas tight sealing between the ACFC sample and the inner wall of the graphite reaction pot. Thereby all the SiO vapor generated in the graphite pot was forced to flow through the porous CFCs during reaction. After reaction, the graphite pot was emptied and mass changes of the pellet and the converted CFCs were measured.

### 3. Characterization

The converted CFC samples were treated with 10% hydrofluoric acid to determine the content of silica possibly formed by condensation of excess SiO vapor generated during reaction. The carbon content in the HF-treated sample was determined by measuring weight change of the sample after burning out unreacted carbon in air at 1123 K for 3 h.<sup>11</sup> The remainder was assumed to represent the SiC in the converted CFC.

The structure of the converted samples was studied by X-ray diffractometry with Cu K $\alpha$  monochromatic radiation. The surface areas and pore size distributions of the samples were determined by multi-point BET and BJH method using nitrogen desorption isotherms, respectively.<sup>10</sup> The mechanical properties of the converted samples were compared by the three-point bending strength test for the 5 mm  $\times$  8 mm  $\times$  15 mm specimen. Measurements were conducted using an universal test instrument (Instron 4302) with a strain rate of 0.5 mm/min and a span length of 11 mm. The microstructure of the samples was examined by scanning electron microscopy.

## III. Results and Discussion

The XRD patterns of the CFCs of different SSA reacted with SiO at 1673 K for 2 h are shown in Fig. 1. As the SSA of CFC increased, the intensity of peaks due to  $\beta$ -SiC ( $2\theta=35.6^\circ$ ,  $60.0^\circ$  and  $71.8^\circ$ ) steadily increased showing the progressive conversion of carbon to SiC. The increase of the peak intensity is due to the formation and simultaneous grain growth of SiC crystallines. A

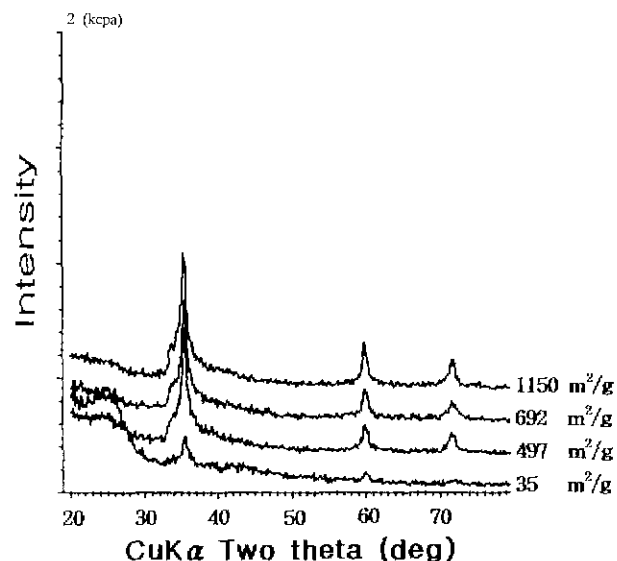


Fig. 1. XRD patterns of converted carbon fiber composites obtained from carbon fiber composites of different specific surface areas.

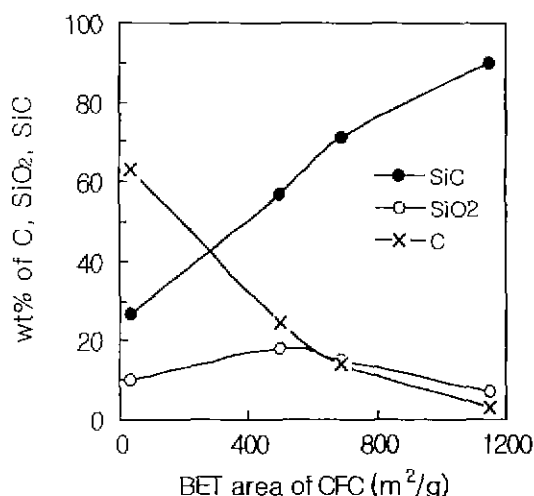
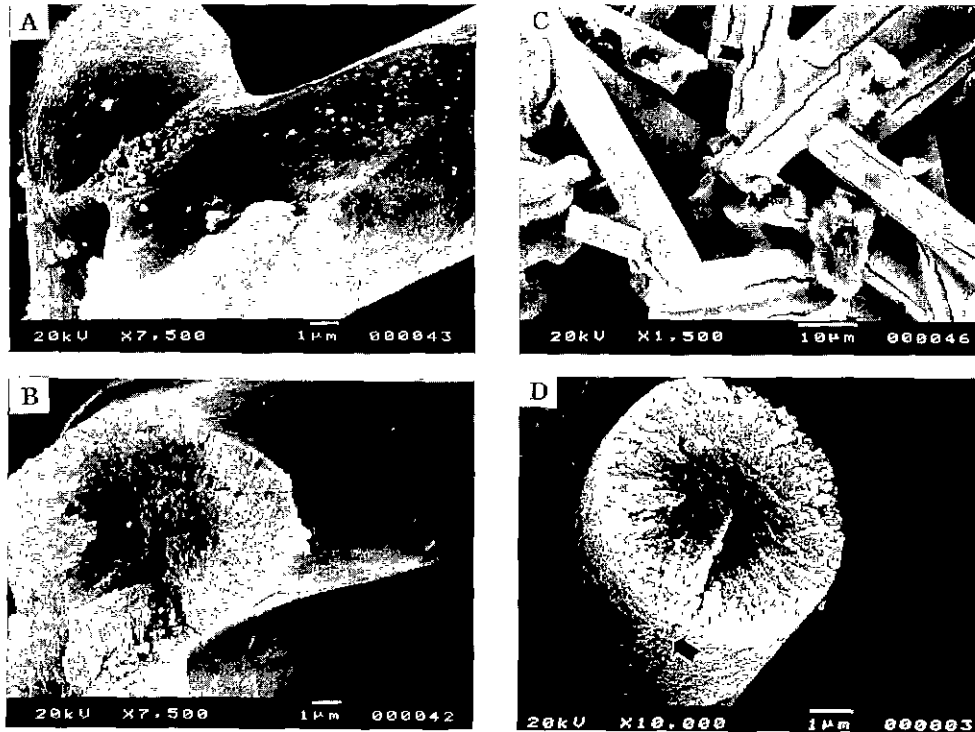


Fig. 2. SiC, C and SiO<sub>2</sub> content in the converted carbon fiber composites as a function of specific surface area of carbon fiber composites.

diffusive pattern at  $2\theta=20\sim 30^\circ$  presumably due to unreacted carbon could be observed for all the samples and grew with decreasing specific surface area of CFC.

Chemical analysis revealed that the converted CFC samples consisted of SiC, C and a substantial amount of silica as plotted in Fig. 2. It is shown that the SiC content increases with SSA of CFC, i.e., 27 wt% for 35-CFC to 90 wt% for 1150-CFC. Clearly, higher SSA favors the conversion of carbon to silicon carbide. Silica in the converted CFC is presumably formed by an excess of SiO vapor condensed back as amorphous phase.<sup>11,12</sup>

SEM micrographs of converted CFCs are shown in Fig. 3. When SiC yield was higher than 57 wt%, cracks developed along axial direction of fiber appeared as



**Fig. 3.** Micrographs of converted carbon fiber composites obtained from carbon fiber composites of different specific surface areas: (A) 35 m<sup>2</sup>/g, (B) 497 m<sup>2</sup>/g, (C) 692 m<sup>2</sup>/g and (D) 1150 m<sup>2</sup>/g.

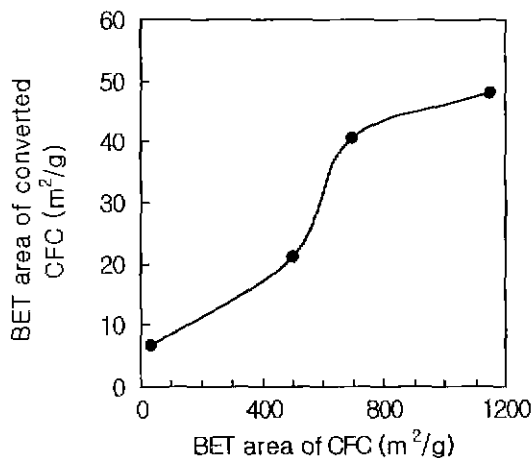
shown by arrows in Fig. 3(C) and (D). These cracks resulted from tensile hoop strain induced by volume decrease of converted carbon as discussed by Ling and Rand who observed the similar radial cracks on their carbon fiber reacted with SiO for 24 hours and longer at 1573 K.<sup>9</sup> It has been known that PAN based carbon fiber has an onion-skin structure on the surface, so called circumferential preferred orientation texture.<sup>10</sup> However, we could not observe any onion-skin type cleavage due to radial shrinkage upon volume reduction. Therefore, it is

postulated that cracks developed on surface of the converted fiber are originated from either surface flaws developed along an axial direction of carbon fiber or radial structure of carbon fiber.<sup>10</sup>

The SSAs of the converted CFCs are shown in Fig. 4. As the SSA of CFC increased from 35 m<sup>2</sup>/g to 1150 m<sup>2</sup>/g, the SSA of converted CFC increased from 7 m<sup>2</sup>/g to 48 m<sup>2</sup>/g. BET measurements of CFC performed before and after heat treatment in vacuum at 1,400°C for 2 hours without SiO-C reaction showed that the specific surface area of the ACFC decreased from 1150 m<sup>2</sup>/g to 500 m<sup>2</sup>/g. Similar reduction of specific surface area dependent on heat treatment has been reported for activated charcoal.<sup>11</sup> Therefore, the specific surface area of converted CFC was more affected by that of CFC than the carbon content in the converted CFC, shown Fig. 2.

Fig. 5 shows the pore size distribution of converted CFCs. CFC before reaction has micropores of dominant pore radius smaller than 2 nm.<sup>9</sup> As the reaction proceeded, micropores were converted to mesopores and the dominant pore radius of the latter increased to about 9 nm. Such an increase was presumed to result from growth of SiC crystallites (Fig. 1) and the volume reduction of carbon converted to SiC as mentioned before.

Fig. 6 shows the variation in bending strength of the converted CFCs as a function of SSA values after conversion reaction. The bending strength of the converted CFCs decreased from about 8.5 MPa to 2.1 MPa with increasing SSA. Therefore the bending strength



**Fig. 4.** Specific surface area of converted carbon fiber composites as a function of that of carbon fiber composites before conversion reaction.

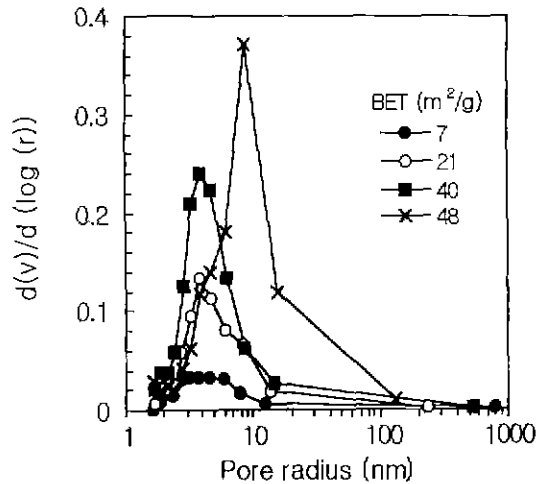


Fig. 5. Pore structure development of converted carbon fiber composites at different level of specific surface area.

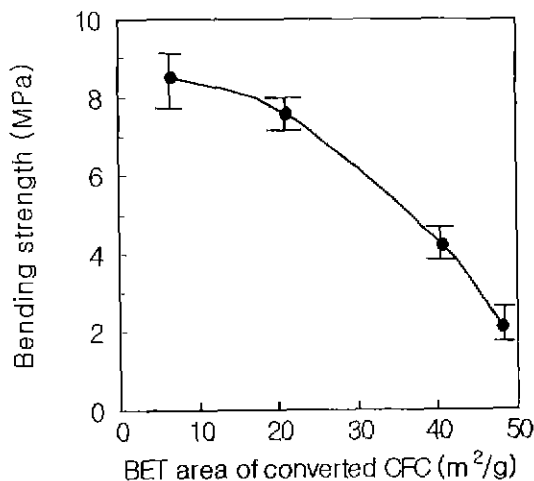


Fig. 6. Bending strength of converted carbon fiber composites as a function of specific surface area.

of the converted CFC appears to decrease with increasing SSA and cracks formed in the converted fibers as shown in Fig. 3.

#### IV. Conclusions

Carbon bonded PAN-based carbon fiber composites with various specific surface areas have been used for the preparation of the silicon carbide bonded silicon carbide fiber composites. It was shown that specific surface area had a significant effect on the degree of conversion of carbon to silicon carbide. All the converted carbon fiber composites have a considerable amount of amorphous silica condensed from SiO vapor generated during conversion process. Crack formation in the converted carbon fiber seems inherent to the texture of PAN-based carbon fiber and degrade the strength of silicon carbide bonded silicon carbide fiber composites.

#### Acknowledgment

The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1997.

#### References

1. P. Kennedy and B. North, "The Production of Fine Silicon Carbide Powder by the Reaction of Gaseous Silicon Monoxide with Particulate Carbon," *Pro. Brit. Ceram. Soc.*, **33**(1) 1-15 (1983).
2. M. J. Ledoux, S. Hantzer, C. P. Huu, J. Guille and M. P. Desaneaux, "New Synthesis and Uses of High-Specific-Surface SiC as a Catalytic Support That Is Chemically Inert and Has High Thermal Resistance," *J. Catal.*, **114**, 176-185 (1988).
3. M. Benaissa, J. Werckmann, J. L. Hutchison, E. Peschiera, J. Guille and M. J. Ledoux, "High-Resolution Transmission Electron Microscopy Study on SiC Grown from SiO and C: Crystal Growth and Structural Characterization," *J. Cryst. Growth*, **131**, 5-12(1993).
4. M. Benaissa, J. Werckmann, G. Ehret, E. Peschiera, J. Guille and M. J. Ledoux. "Structural Studies of Active Carbon Used in the Growth of Silicon Carbide Catalyst Support," *J. Mat. Sci.*, **29**, 4700-4707 (1994).
5. R. Moene, J. Schoonman, M. Makkee and J. A. Moulijn, "Nickel Catalyzed Conversion of Activated Carbon into Porous Silicon Carbide," *Mat. Res. Soc. Symp. Proc.*, **368**, 75-80 (1995).
6. K. Okada, H. Kato and K. Nakajima, "Preparation of Silicon Carbide Fiber from Activated Carbon Fiber and Gaseous Silicon Monoxide," *J. Am. Ceram. Soc.*, **77**(6) 1691-1693 (1994).
7. Z. Ling and B. Rand, "Conversion/Coating of Carbon Fibers by Reaction with SiO(g)," *Pro. Brit. Ceram. Soc.*, **54**, 31-40 (1995).
8. J. C. Lee et. al, "The Effect of Carbonization Temperature of PAN Fiber on the Properties of Activated Carbon Fiber Composites," *Carbon*, **35**, 1479-1484 (1997).
9. O. Kubaschewski and T. G. Chart, "SiO Pressures due to the Reaction between Solid Si and SiO<sub>2</sub>," *J. Chem. Thermodynamics*, **6**(5) 467-476 (1974).
10. L. P. Rist and D. P. Harrison, "Surface Area and Pore Development During Lignite Activation," *Fuel*, **64**, 291-302 (1985).
11. G. W. Brady, "A Study of Amorphous SiO<sub>2</sub>," *J. Phys. Chem.*, **63**(7) 1119-20 (1959).
12. B. Friede and M. Jansen, "Some Comment on so-called Silicon Monoxide," *J. Non-Cryst. Solids*, **204**, 202-203 (1996).
13. T. Belmonte, L. Bonnetain and J. L. Ginoux, "Synthesis of Silicon Carbide Whiskers Using the Vapor-Liquid-Solid Mechanism in a Silicon-Rich Droplet," *J. Mat. Sci.*, **31**, 2367-71 (1996).
14. J. B. Donnet and R. C. Barsal, *Carbon Fibers*, pp. 92-96, Marcel Dekker Inc., New York & Basel, 1984.
15. K. Kogure and G. Sinos, "Microstructure and Texture of Pitch-Based Carbon Fiber After Creep Deformation," *Carbon*, **32**(8) 1469-1484 (1994).