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Pitch-based carbon fiber reinforced SiC composites for space optics

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Abstract—One of the key technologies for the next generation space telescope with a large-scale reflector is a material having high strength-to-weight ratio, high stiffness-to-weight ratio, and low coefficient of thermal expansion. Pitch-based carbon fiber reinforced SiC composites were developed to comply with such requirements. Two types of C/C substrates were prepared and carbonization and graphitization conditions were evaluated. Siliconization conditions were also studied to find better conditions to obtain favorable phase composition of the composites. Mechanical performance as measured in bending strength and fracture toughness tests was significantly improved. Thermal expansion behavior and roughness of the polished surface of these composites were also determined to be sufficient for space infrared mirror applications.

1. INTRODUCTION

In this decade, several new projects for development of a space telescope have been studied. Most of the projects include large-scale reflectors over 3 m of aperture to collect faint light from deep space. The reflector has to be light enough in weight to be launched. Precise control of the shape of the reflector surface is also required to obtain high resolution. One of the key technologies for such a reflector is a material having high strength-to-weight ratio, high stiffness-to-weight ratio, and low coefficient of thermal expansion. High thermal conductivity is also preferred. Several candidates such as fused silica, beryllium, silicon carbide and carbon fiber reinforced composites have been evaluated [1–4].

C/SiC composites formed by means of liquid silicon infiltration have also been developed for large space optics [5, 6]. The liquid silicon infiltration process

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is a fast and low-cost manufacturing process for structural components. Small shrinkage during the silicon infiltration into C/C substrates allows machining of C/C substrates to fabricate final component shape. The mechanical, thermal, thermo-mechanical behavior obtained has been sufficient to fabricate a large-scale optical mirror whose aperture diameter is more than 3 m.

However, conventional C/SiC composites for space optics have been reinforced by PAN-based or rayon-based carbon fibers that react easily with silicon during liquid silicon infiltration. As the number and size of the residual carbon fibers decreases, the strength and the fracture toughness of composites will also decrease. A reinforcing fiber more resistant to reaction with silicon would result in higher strength and fracture toughness retention, and thus a lighter weight mirror.

Generally, pitch-based carbon fibers have high resistance to reaction with metals including silicon. The difference in the reactivity of pitch-based carbon reinforcing fibers and carbon matrix is favorable to control the reaction to form an appropriate silicon carbide. Recently, the reaction of liquid silicon with carbon has been studied, including a kinetics model of the reaction [7] and the infiltration behavior of liquid silicon using Darcy's law [8]. Such studies suggest the possibility of fabricating an optimized composite composed of effective fiber reinforcement and substantial silicon carbide matrix.

In this study, new C/SiC composites reinforced by pitch-based carbon fibers were fabricated to improve the mechanical performance of C/SiC composites for space optics. The process conditions including carbonization, graphitization, and liquid silicon infiltration (or siliconization) were examined. Mechanical, thermal and optical properties were evaluated comparing with conventional C/SiC composites.

2. EXPERIMENTAL

2.1. Fabrication of C/SiC composites

Figure 1 shows the fabrication process of C/SiC composites. The process is composed of three steps: (1) preparation of carbon fiber preform; (2) carbonization and graphitization; (3) liquid silicon infiltration. In the carbonization process, the substrates may be re-impregnated with carbon precursors and re-carbonized to increase matrix carbon ratio in the C/C substrates.

2.1.1. Preforms for C/C substrates. Two types of carbon preforms were prepared in this study. Type A was composed of pitch-based milled fibers (Mitsubishi Chemical) whose Young's modulus was about 600 GPa. The average length of the fibers was 0.2 mm and the volume fraction of fibers was about 35%. Type B composed of pitch-based short fibers (Mitsubishi Chemical) whose Young's modulus was about 240 GPa. The average length of the fibers was 30 mm and the volume fraction of fibers was about 40%. In both types, fibers were oriented randomly in the preforms.

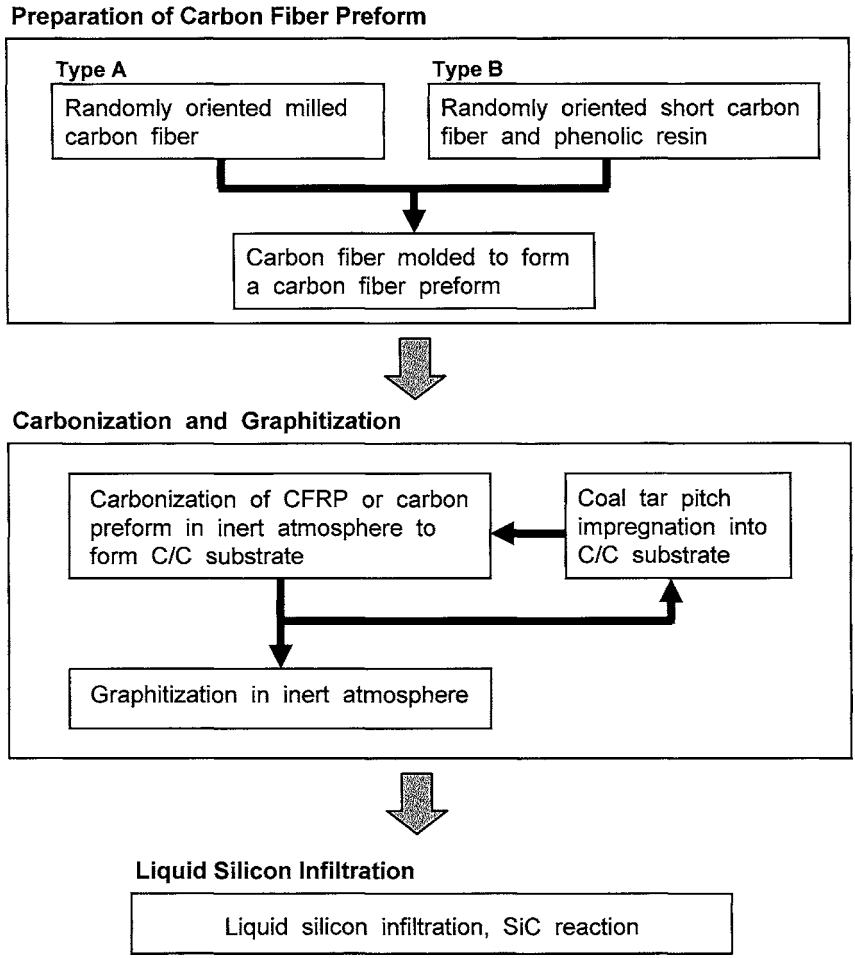


Figure 1. Fabrication process of pitch-based C/SiC composites.

2.1.2. Carbonization and graphitization process. Coal tar pitch was impregnated into the type A preform, which was carbonized at 973 K in an inert atmosphere. Some preforms were re-impregnated and re-carbonized up to three times. Then the carbonized preforms were heat treated in 2273 K or 3073 K in an inert atmosphere.

Phenolic resin was impregnated into the type B preform to produce a CFRP substrate. The CFRP was then heat treated in 2273 K or 3073 K in an inert gas atmosphere. No re-impregnation was performed for the type B preform.

2.1.3. Liquid siliconization of C/C substrates. Liquid silicon was infiltrated into the C/C substrates and reacted with the carbon matrix to form silicon carbide in vacuum. Three reaction temperatures, 1873 K, 1973 K, and 2073 K were examined. The temperature was increased at a rate of 5 K/min. The duration time at reaction

temperature was 30 min in each case. Only in the case of 1973 K, a longer duration time was also examined.

2.2. Analysis of the microstructure

Optical microscopy and scanning electron microscopy were used to analyze the microstructure of the composites. Small samples were cut off the pitch-based C/SiC composites and mounted in polyester resin. The samples were then roughly polished with #220 sandpaper and lapped with a diamond and finished by buffing. The phase composition was evaluated by image analysis of the micrograph.

2.3. Mechanical performance

2.3.1. Bending strength. An Instron 1185 universal test machine was used to evaluate the mechanical performance of the composites. A four-point bending test based on JIS R1601 was performed to evaluate the bending strength. The size of the specimen was 40.0 mm (l) × 4.0 mm (w) × 3.0 mm (t), and the upper and the lower support spans were 10.0 mm and 30.0 mm, respectively. The crosshead speed was 0.5 mm/min.

2.3.2. Fracture toughness, K1C. The single edge notched beam method was applied to measure the K1C value. The size of the specimen was 40.0 mm (l) × 4.0 mm (w) × 3.0 mm (t). The depth of the notch was 0.45 mm. A three point bending configuration was used, in which the support span was 16.0 mm. The crosshead speed was 0.5 mm/min.

2.4. Thermal expansion

A thermal expansion analyzer LIX-1 (Shinku-Riko) was employed to determine the coefficient of thermal expansion (CTE) of the composites. This laser interferometer-based apparatus has an accuracy of 0.1 ppm/K. The C/SiC composites were cut into sharp pointed specimens, as shown in Fig. 2. The size of the specimen was 15.0 mm (l) × 5.0 mm (w) × 3.0 mm (t). Temperature range in the test was from 100 K up to 353 K. Heat-up rate was 2°C/min.

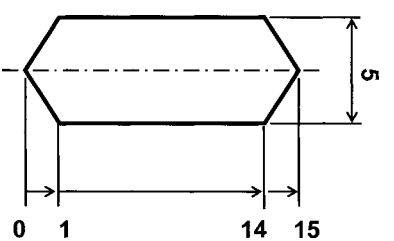


Figure 2. Specimen for CTE measurement.

2.5. Evaluation of optical surface

The specimens were ground with a diamond lapping film and buffed with 1 micron diamond abrasive. The size of the specimen was 100.0 mm (l) × 50.0 mm (w) × 10.0 mm (t). Local surface roughness was evaluated with a DEKTAK 3030 surface profile measuring system (Sloan Technical Corp.). Five lines of 250 micron on every specimen were selected randomly and surface height was scanned.

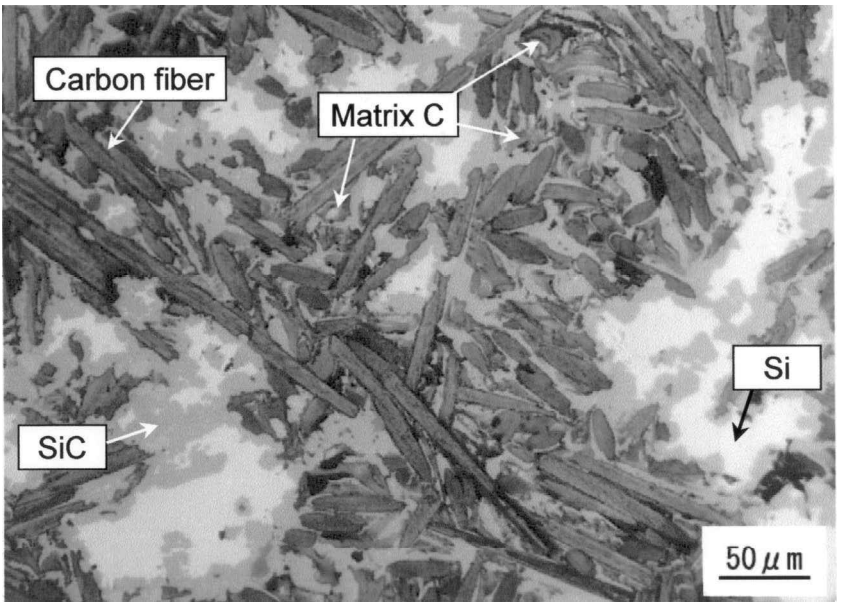
3. RESULTS AND DISCUSSION

3.1. Dependence of microstructure on process conditions (Type A)

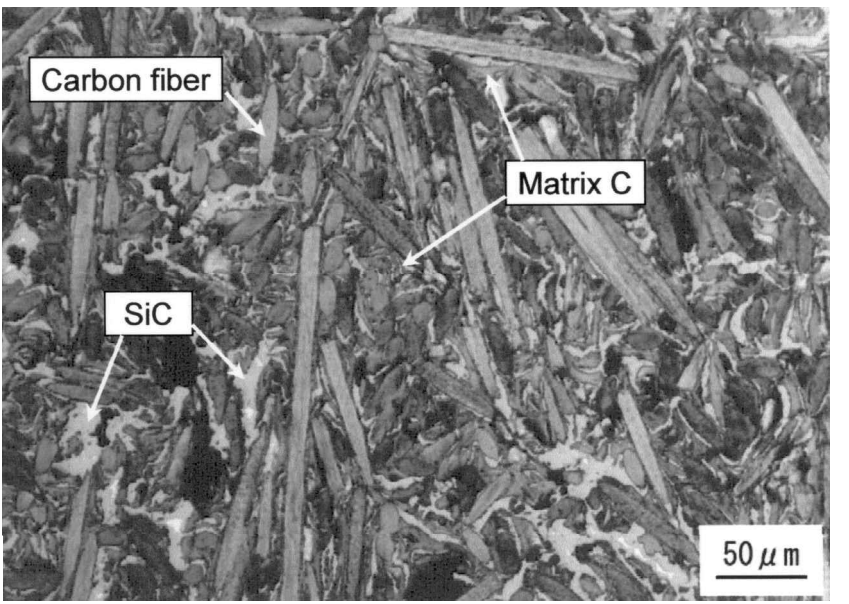
3.1.1. Dependence on carbonization conditions. Figure 3 shows micrographs of the C/SiC composites made from Type A C/C substrates with varying numbers of re-impregnation and re-carbonization cycles. The liquid siliconization temperature was 1873 K. In Fig. 3a, silicon carbide (gray sections) is observed around carbon fibers, and residual free silicon (white sections) is embedded within the silicon carbide. A small amount of residual carbon matrix is also observed just around carbon fibers. When the substrate was re-impregnated and re-carbonized, the residual carbon matrix area increased while silicon carbide decreased. The composition of the C/C substrate as calculated from material density is listed in Table 1. Since the volume of the matrix increases about 2.19 times due to reaction with silicon, the substrate without re-impregnation has enough capillary volume for the reacted SiC matrix and also for residual free silicon. When the C/C substrate was re-impregnated once, the capillary volume was slightly less than required to support the carbon–silicon reaction, which leads to residual carbon matrix in the C/SiC composites, as shown in Fig. 3b. The residual carbon matrix is estimated to be about 6%. The C/C substrate shown in Fig. 3c was re-impregnated twice; its phase composition is almost same as in Fig. 3b. The residual carbon matrix is estimated to be about 18% in this case. However, too much reaction between carbon matrix and silicon occurred, leading to fracture of the composite as shown in Fig. 4.

3.1.2. Dependence on siliconization temperature and duration time. Figure 5 shows micrographs of C/SiC composites made from Type A C/C substrates for varying siliconization temperatures. Almost the same phase microstructures were observed in the case of 1873 K and 1973 K. However, a small amount of unimpregnated area is also observed in the case of 1873 K. When the temperature was 2073 K, more reaction between the carbon matrix and silicon occurred. Consequently, a thicker silicon carbide phase is observed in Fig. 5c.

Figure 6 shows micrographs of C/SiC composites made from Type A C/C substrates at 1973 K siliconization temperature and 5 h duration time. The silicon carbide area is thick as was observed in Fig. 5c. The result that higher temperature and longer duration time leads to more reaction between the carbon matrix and the

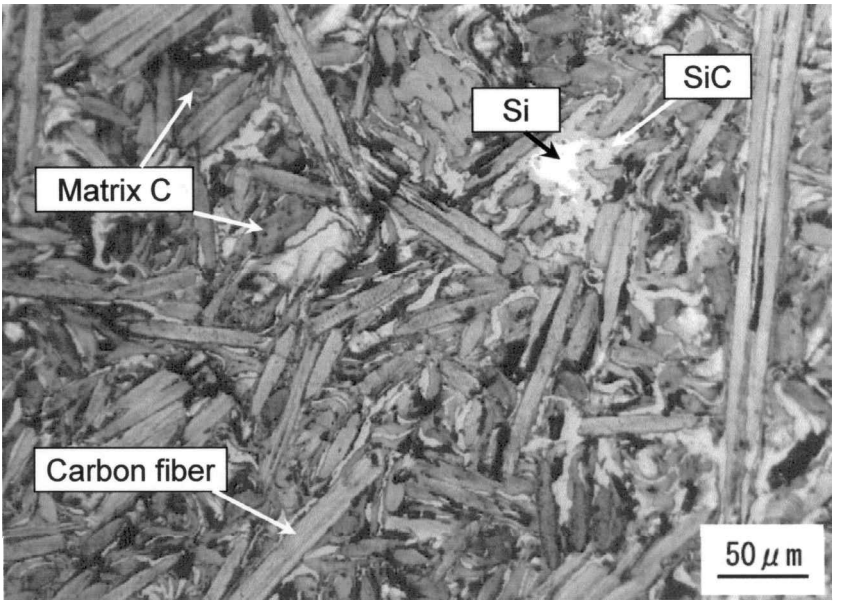


(a)



(b)

Figure 3. Micrographs of the C/SiC composites (Type A, siliconized at 1873 K). (a) No re-impregnation. (b) One re-impregnation. (c) Two re-impregnations.



(c)

Figure 3. (Continued).

Table 1.
The composition of the C/C substrate

Re-impregnation cycles	Density (g/cm^3)	Fiber volume (vol%)	Carbon matrix (vol%)	Void (vol%)
0	1.15	35	19.8	45.2
1	1.43	35	33.1	31.9
2	1.56	35	39.8	25.2

impregnated liquid silicon agrees well with previous work [7]. Reaction between the carbon fiber and the impregnated silicon, however, was not observed in the above conditions.

3.1.3. Dependence on graphitization temperature. Figure 7 shows micrographs of Type A C/C substrates graphitized at different temperatures. During the carbonization process, residual carbon matrix out of the precursors was unevenly distributed just around and between carbon fibers. In the graphitization process, additional shrinkage of the carbon matrix occurs and some cracks grow between the carbon fibers and the matrix carbon or within the carbon matrix in Fig. 7a. When the graphitization temperature increases up to 3073 K, remarkable cracks at the interfaces between the carbon fibers and matrix carbon are observed in Fig. 7b. These cracks should become good capillary channels for liquid silicon infiltration and reaction area in the siliconization process should increase. A micrograph of a

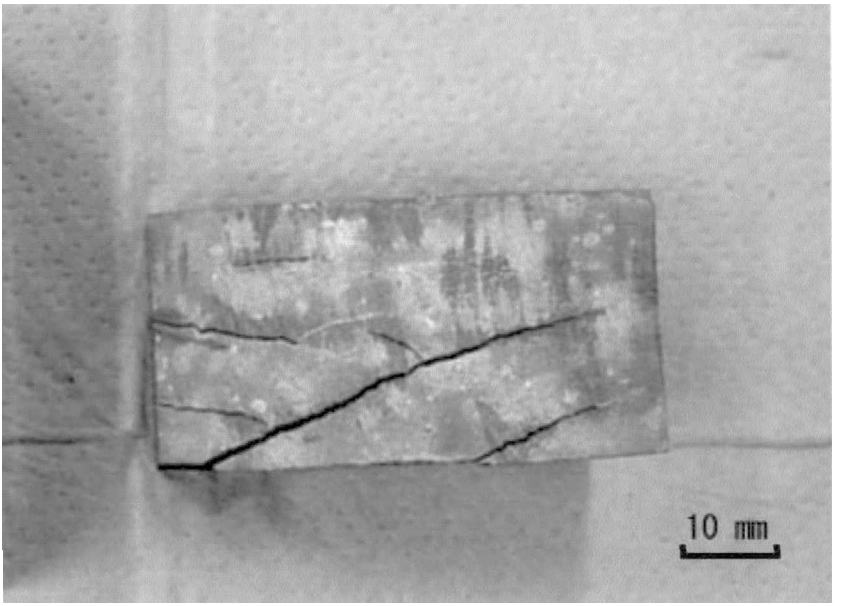


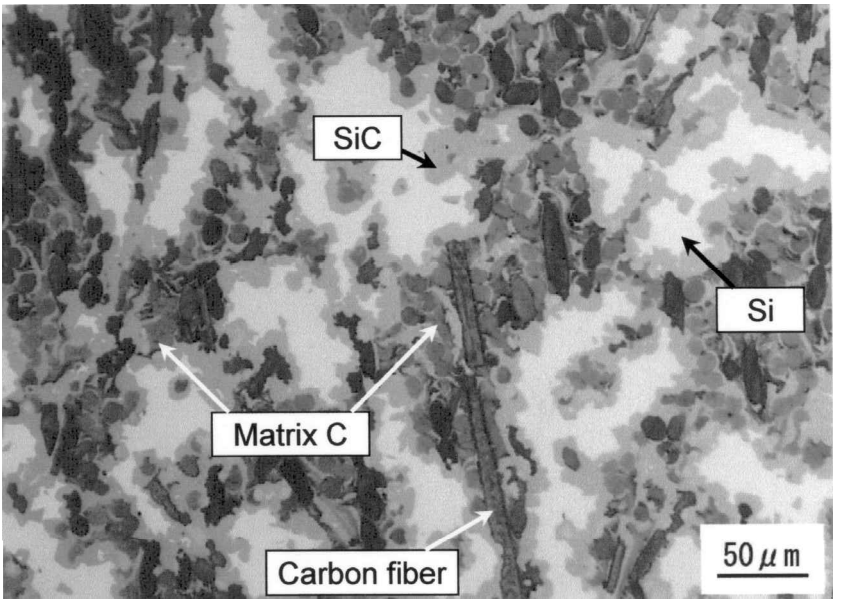
Figure 4. C/SiC composite specimen with excess reaction.

C/SiC composite using a C/C substrate graphitized at 3073 K is shown in Fig. 8. Processing conditions other than the temperature of graphitization were the same as the composites in Fig. 6. In Fig. 8, more silicon carbide is observed than in Fig. 6. In addition, some carbon fibers have also reacted with the silicon carbide, which means excess heat treatment during the graphitization should lead to excess reaction in siliconization process.

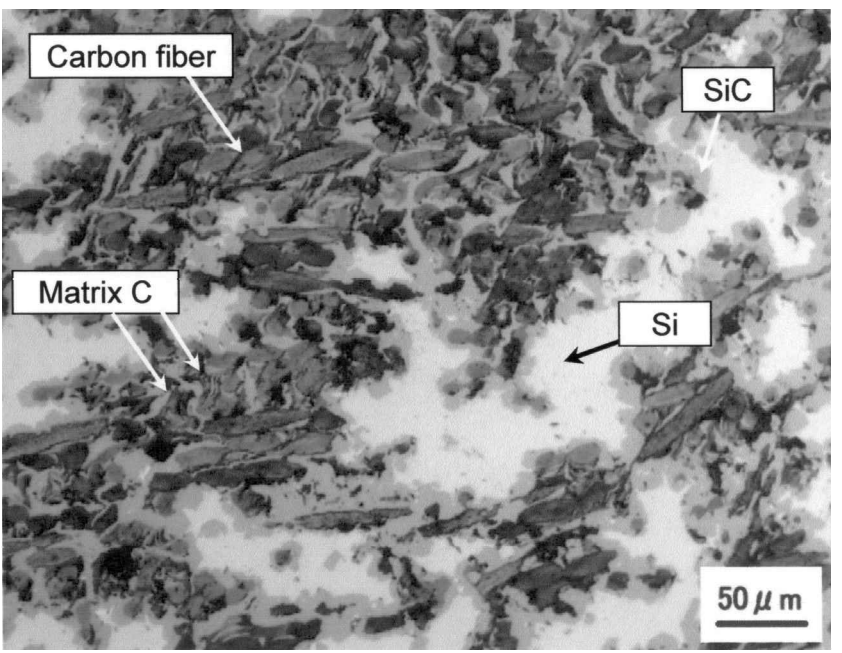
3.1.4. Comparison with C/SiC composites reinforced by rayon-based carbon fiber. Figure 9 shows a typical cross sectional view of a conventional C/SiC composite reinforced by rayon-based carbon fiber. Rayon-based carbon fibers exhibit significant reaction with hot liquid silicon. In the micrograph, a small amount of residual carbon fiber is observed. Considerable free silicon is also observed. Decreased numbers of reinforcing fibers and a lot of free silicon is expected to decrease the strength of the composite. In contrast, the pitch-based carbon fiber reinforced silicon carbide composites have more residual reinforcement. When sufficient silicon carbide matrix is obtained and the amount of the free silicon is minimized, the composites should have more strength and toughness.

3.2. Dependence of microstructure on process conditions (Type B)

Since the Type B preform has a higher volume fraction of carbon fiber, re-impregnation was not carried out. Dependence of microstructure on siliconization temperature and graphitization temperature was examined.



(a)



(b)

Figure 5. Micrographs of the C/SiC composites (Type A). (a) Siliconized at 1873 K. (b) Siliconized at 1973 K. (c) Siliconized at 2073 K.

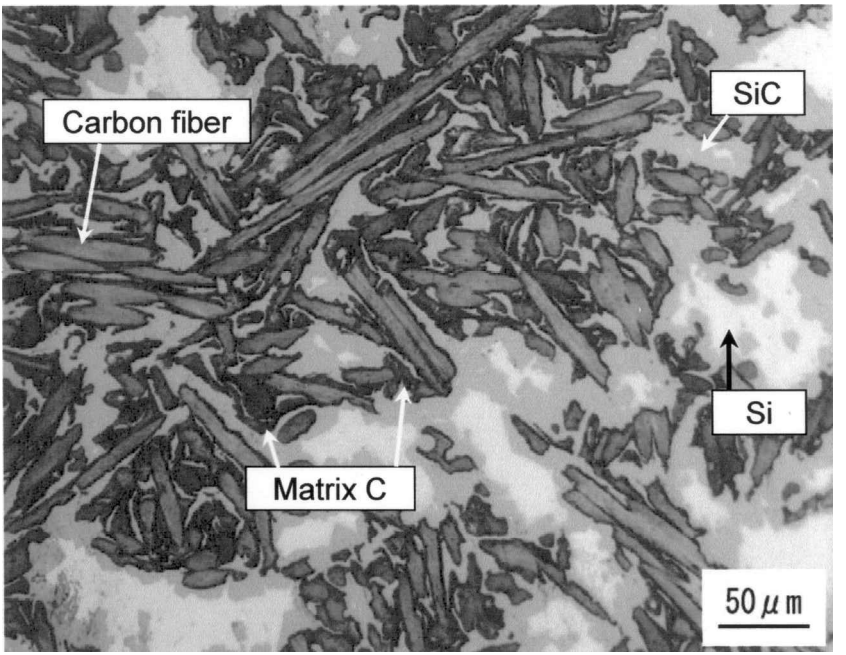


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Figure 5. (Continued).

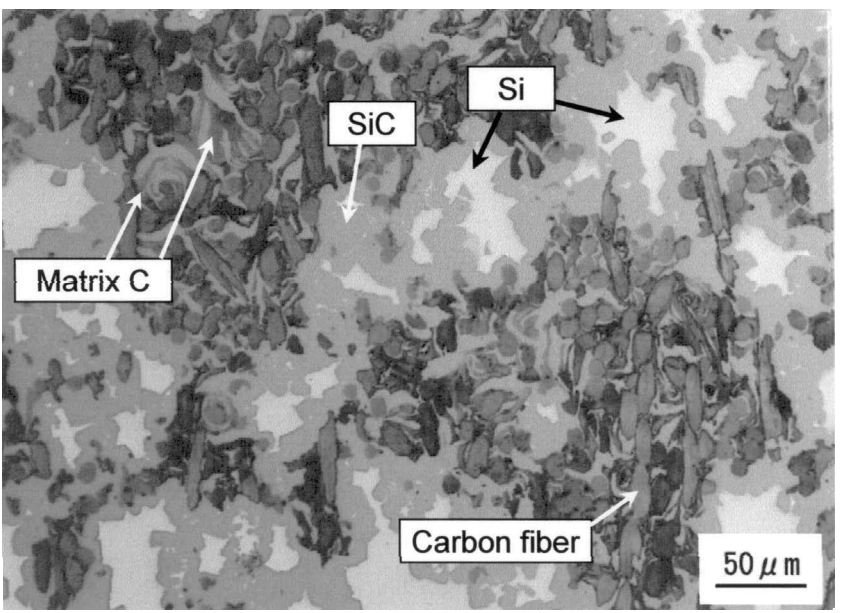
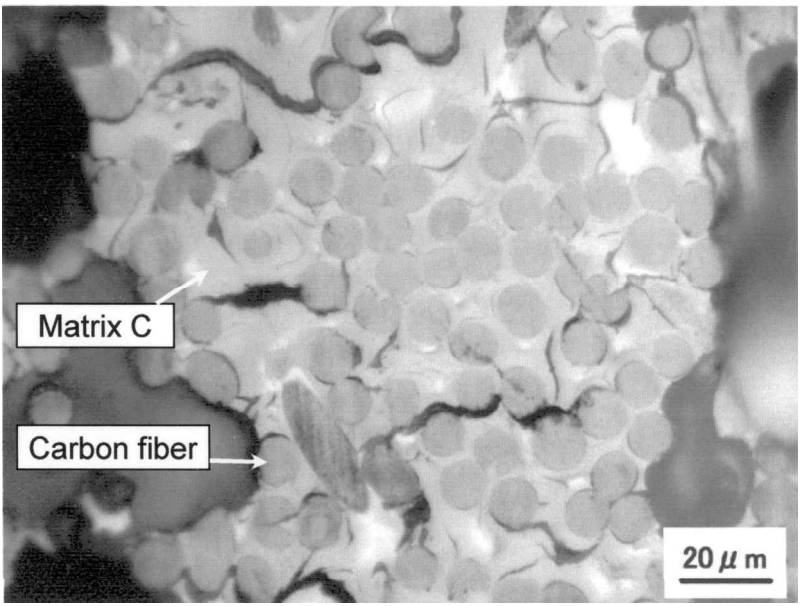
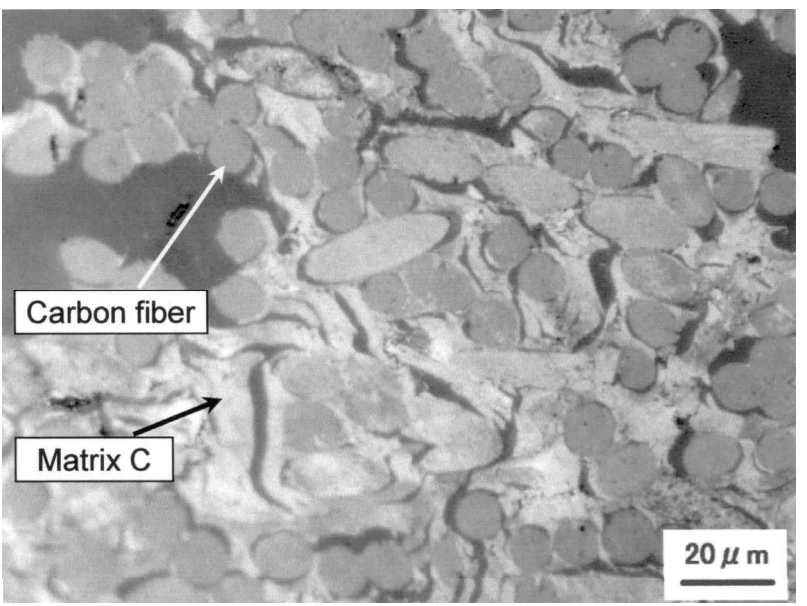


Figure 6. Micrograph of C/SiC composites (Type A, siliconized at 1973 K and 5 h duration).



(a)



(b)

Figure 7. Micrographs of Type A C/C substrates. (a) Graphitized at 2273 K. (b) Graphitized at 3073 K.

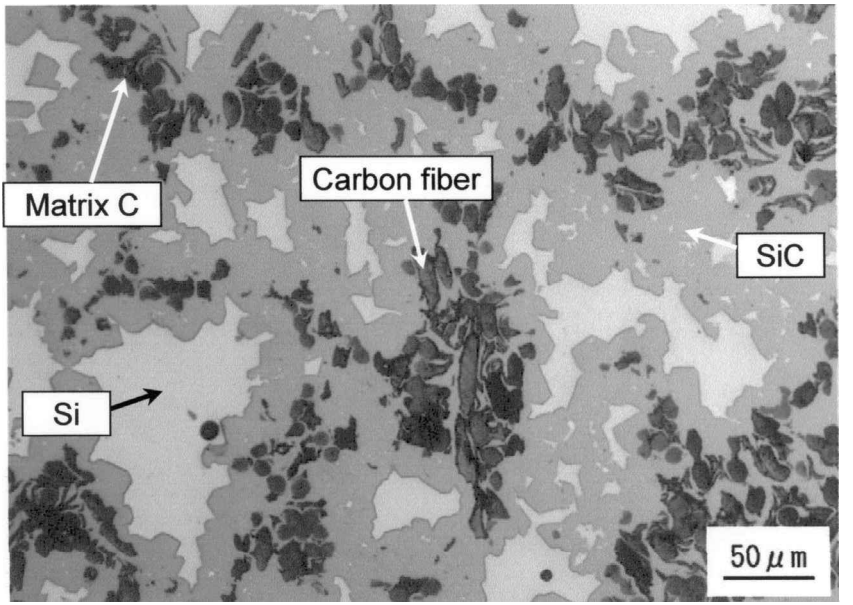


Figure 8. Micrograph of a C/SiC composite using a Type A C/C substrate graphitized at 3073 K.

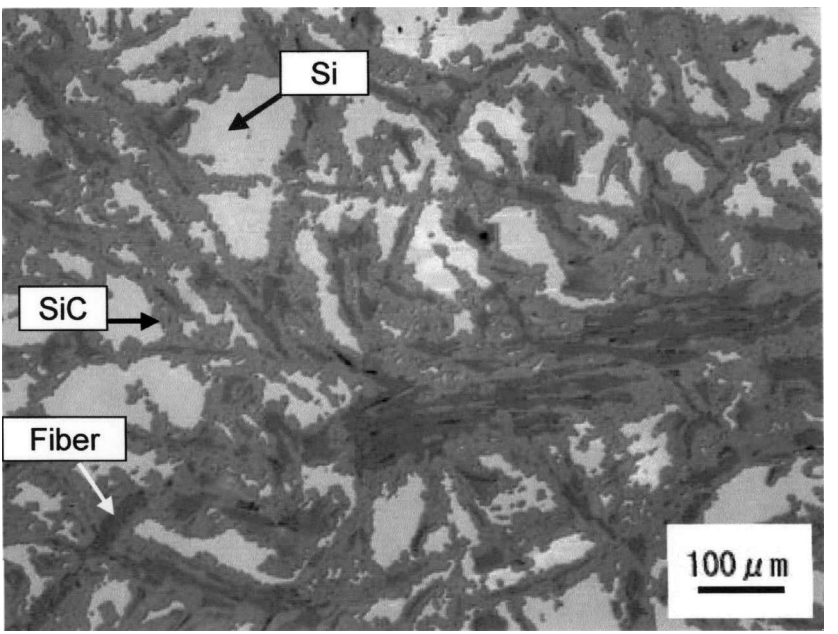
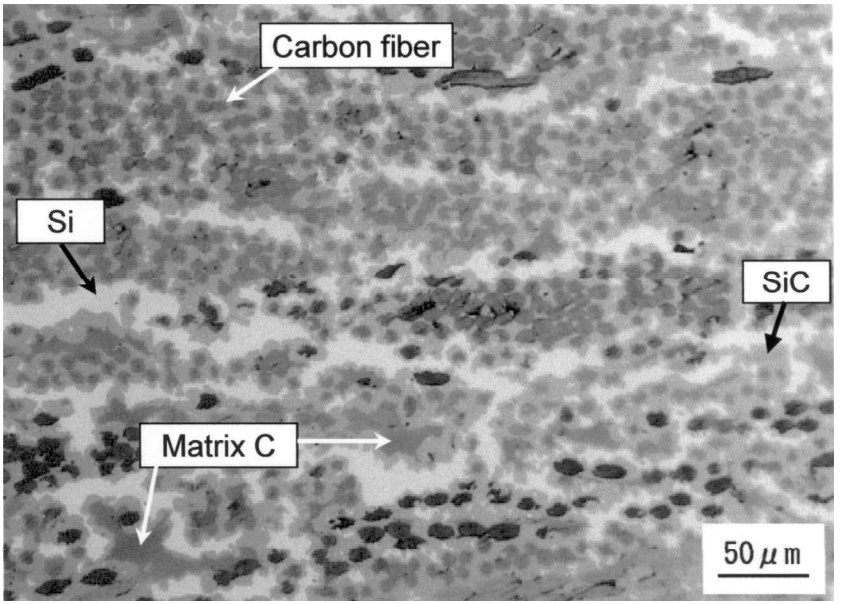
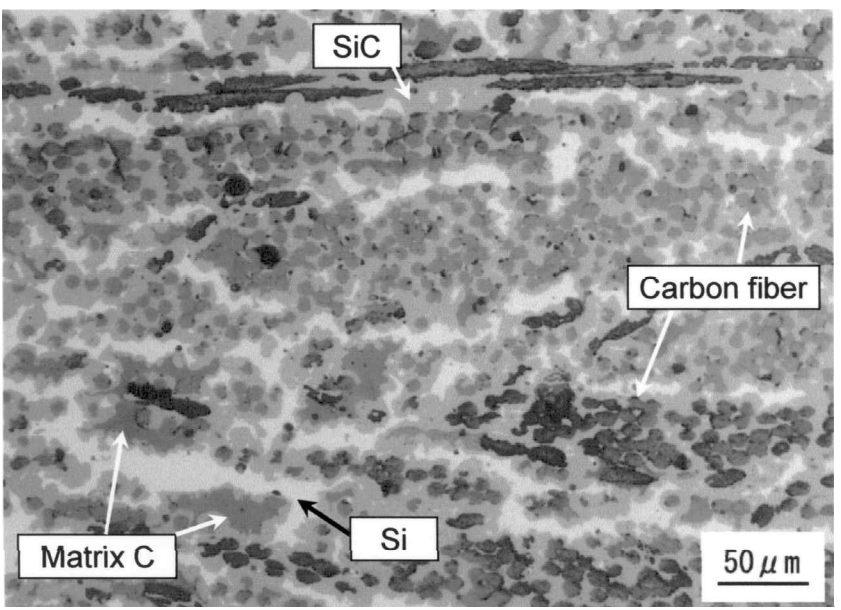


Figure 9. Micrograph of a conventional C/SiC composite reinforced by rayon-based carbon fiber.

3.2.1. Dependence on siliconization temperature and duration time. Figure 10 shows micrographs of C/SiC composites made from Type B C/C substrates at varying siliconization temperatures. The same tendency as in the case of Type A

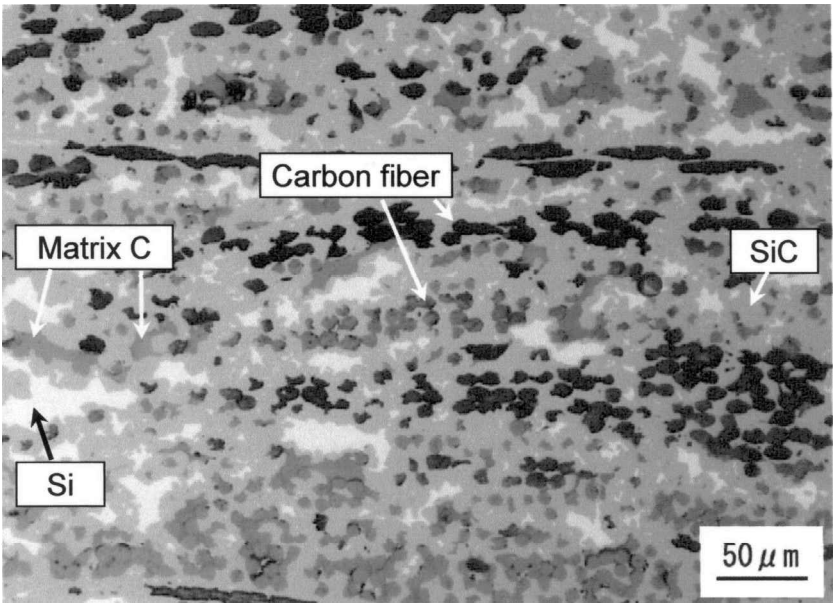


(a)



(b)

Figure 10. Micrographs of the C/SiC composites (Type B). (a) Siliconized at 1873 K. (b) Siliconized at 1973 K. (c) Siliconized at 2073 K.



(c)

Figure 10. (Continued).

substrates was observed. When the siliconization temperature was 1873 K and 1973 K, the C/SiC composites were composed of carbon fibers, silicon carbide, and residual silicon. The phase composition and the specific gravity was almost the same for these cases. In the case of treatment at 2073 K, the amount of silicon carbide increased, which resulted in a higher specific gravity for this composite.

Dependence on the duration time is compared in Fig. 11. When the substrate was siliconized at 1973 K for 5 h, the amount of silicon carbide was much more than the previous cases. However, some carbon fibers also reacted with the liquid silicon as shown in Fig. 11a. When the duration time was 3 hours, reaction of carbon fibers was prevented and much silicon carbide was obtained in Fig. 11b.

3.2.2. Dependence on graphitization temperature. One of the Type B C/C substrates was also graphitized at 3073 K. Such substrates include many cracks between the carbon fibers and matrix carbon, which caused excess reaction of carbon fiber with the silicon carbide. Typical phase composition is shown in the micrograph of Fig. 12.

3.3. Mechanical performance

3.3.1. Bending strength. The results of the four-point bending strength tests are listed in Table 2. The highest mean strength was obtained in Type A composites when the siliconization temperature was 1973 K and the duration time was 5 h. The standard deviation of the strength of this material was less than 5 MPa

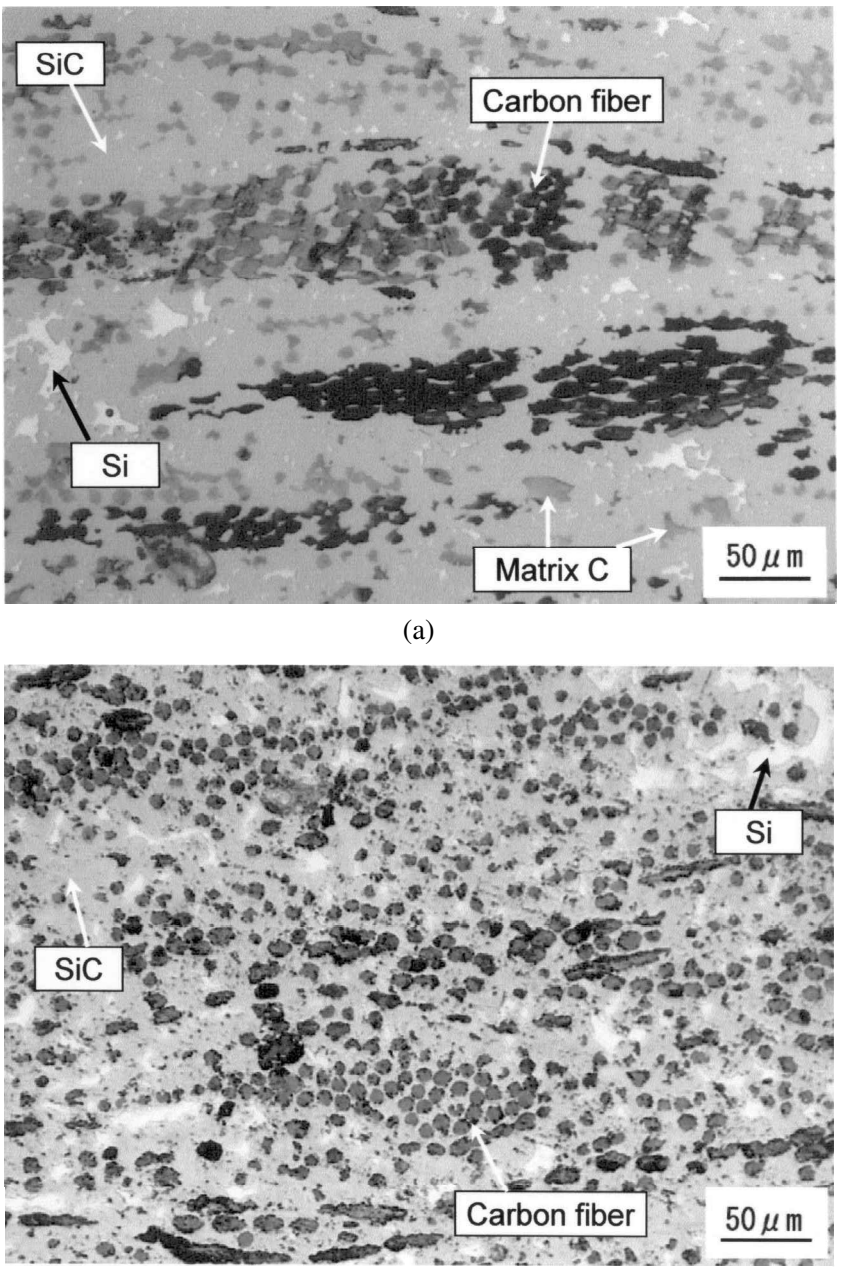


Figure 11. Micrographs of the C/SiC composites (Type B, siliconized at 1973 K). (a) Five hours duration. (b) Three hours duration.

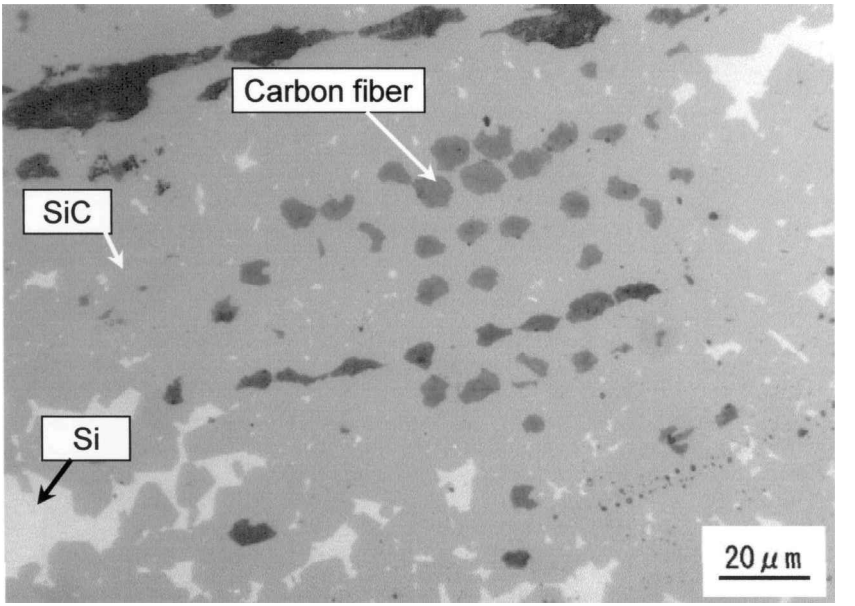


Figure 12. Micrograph of a C/SiC composite using a Type B C/C substrate graphitized at 3073 K.

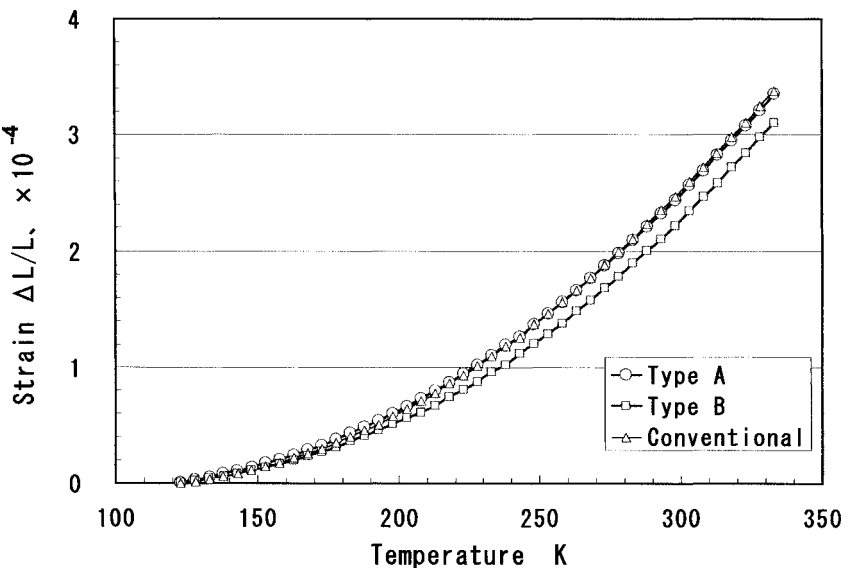


Figure 13. Thermal expansion of C/SiC composites.

corresponding to 2.9% of the mean value, which leads to the high value of the strength allowable. The best mean value obtained in Type B composites was 205 MPa when the siliconization temperature was 1973 K and the duration time was 3 h. The standard deviation of the strength of this material was less than 5%.

Table 2.
Four point bending strength of C/SiC composites

	Mean (MPa)	Standard deviation (MPa)	Strength allowable (MPa)
Type A	173.2	4.98	144.6
Type B	205.0	9.57	150.1
Conventional	157.7	14.11	76.7

Survival of reinforcing carbon fibers in the composites is considered to be effective to reduce scattering of the strength of these composites.

When designing structures, the allowable stress that can be applied is a function not only of the mean strength, but also of the data scatter. The A-basis allowable in MIL-HDBK-17 is a standardized statistical method in which the material strength is reduced to account for the data scatter. As shown, increasing the silicon carbide matrix yield while minimizing reaction with the reinforcing fibers results in allowable strengths for these two composites that are about twice that of conventional C/SiC composites.

3.3.2. Fracture toughness, K1C. The K1C values of pitch-based carbon fiber reinforced silicon carbide were in the range from 3.3 to 4.0 MPa $m^{1/2}$, while the value of the conventional C/SiC composites is 2.5 MPa $m^{1/2}$. Prevention of reaction of the carbon fibers with the silicon carbide matrix contributes to the improvement of fracture toughness. K1C is important to design an ultra lightweight large-scaled reflector because it corresponds to damage tolerance of a structure. In an actual reflector, it is impossible to fabricate without any small defects. Such defects lead to fracture during handling and mechanical tests, such as vibration and acoustic test on ground or during launch. Material having high damage tolerance enables design of a thinner, lighter reflector structure.

3.4. Thermal expansion behavior

Thermal deformations of C/SiC composites *versus* temperature are shown in Fig. 13. The behavior of Type A composites was almost the same as a conventional composite. In Type B composites, whose volume fraction of carbon fiber is higher than Type A, the coefficient of thermal expansion (CTE) at room temperature was 2.3 ppm/K, which was a little smaller than the 2.4 ppm/K of the conventional composite. Since the CTE of silicon carbide is 3.2 ppm/K, an increase of silicon carbide in the composition should lead to an increase of CTE of the composite. However, though the volume fraction of the silicon carbide in the matrix of the pitch-based fiber reinforced composites was higher, they contained a higher volume of fibers with −1.2 ppm/K longitudinal CTE, and the fibers were less susceptible to reaction with the silicon infiltrate. These factors combined to maintain the CTE values at the same level or lower than the conventional composite.

Table 3.
Small-scale roughness changes measured on the polished composites

	R(a) (nm)
Type A	39.8
Type B	21.1
Conventional	49.2

3.5. Evaluation of optical surface

Small-scale roughness changes measured on the polished composites are listed in Table 3. The Type B composites exhibited an average roughness of 21 nm, which is considerably smoother than conventional composites. The roughness of the Type A composites was also smoother.

Generally, the requirement for surface roughness is approximately 0.05% of the wavelength. Both composites, therefore, were found to be suitable materials for infrared reflectors.

4. CONCLUSIONS

Pitch-based carbon fibers were introduced as reinforcements of C/SiC composites for space optics to improve material strength. Two types of C/C substrates were prepared, and carbonization and graphitization conditions were evaluated. Siliconization conditions were also studied to find better conditions to obtain favorable phase composition of the composites. Mechanical performance as measured in bending strength and fracture toughness tests was significantly improved. Thermal expansion behavior and roughness of the polished surface of these composites were also determined to be sufficient for space infrared mirror applications.

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REFERENCES

1. A. Novi, G. Basile, M. Ghigo, A. Caso, G. Cattaneo and Svelto, Lightweight SiC foamed mirrors for space applications, *Proc. SPIE* **4444**, 59–65 (2001).
2. T. Reed, S. E. Kendrick, R. J. Brown, J. B. Hadaway and D. Byrd, Final results of the subscale beryllium mirror demonstrator (SBMD) program, *Proc. SPIE* **4451**, 5–13 (2001).
3. B. Catanzaro, J. A. Thomas, D. Small, R. Johnston, D. Barder, S. Connell, S. Whitmore and E. Cohen, Optical meteology for testing an all-composite 2-meter diameter mirror, *Proc. SPIE* **4444**, 207–223 (2001).
4. G. B. Hardman, T. J. Heydenburg and R. A. Rockwell, Design comparison of glass and beryllium AMSD mirrors, *Proc. SPIE* **4198**, 213–220 (2001).

5. H. Mucha, A. Kamiya and B. Wielage, Structural evolution of C/C-SiC composites through the main production steps on the liquid silicon infiltration (LSI) route, *Proc. ICCM-11* **II**, 717–724 (1997).
6. C. Muller, U. Ppenburg, W. A. Goodman and M. Jacoby, C/SiC high precision lightweight components for optomechanical applications, *Proc. SPIE* **4198**, 249–259 (2001).
7. H. Zhou and R. N. Singh, Kinetics model for the growth of silicon carbide by the reaction of liquid silicon with carbon, *J. Am. Ceram. Soc.* **78**, 2456–2462 (1995).
8. F. H. Gern, Liquid silicon infiltration: description of infiltration dynamics and silicon carbide formation, *Composites Part A* **28A**, 355–364 (1997).