

Thermal and mechanical properties of C/SiC composites fabricated by liquid silicon infiltration with nitric acid surface-treated carbon fibers

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Carbon fiber reinforced SiC composites (C/SiC) have high-temperature stability and excellent thermal shock resistance, and are currently being applied in extreme environments, for example, as aerospace propulsion parts or in high-performance brake systems. However, their low thermal conductivity, compared to metallic materials, are an obstacle to energy efficiency improvements via utilization of regenerative cooling systems. In order to solve this problem, the present study investigated the bonding strength between carbon fiber and matrix material within ceramic matrix composite (CMC) materials, demonstrating the relation between the microstructure and bonding, and showing that the mechanical properties and thermal conductivity may be improved by treatment of the carbon fibers. When fiber surface was treated with a nitric acid solution, the observed segment crack areas within the subsequently generated CMC increased from 6 to 10%; moreover, it was possible to enhance the thermal conductivity from 10.5 to 14 W/m·K, via the same approach. However, fiber surface treatment tends to cause mechanical damage of the final composite material by fiber etching.

Key words: C/SiC composites, LSI process, Surface treatment, Thermal conductivity, Mechanical properties.

Introduction

Scramjet engines are capable of longer-range flight than rocket propulsion and are attracting attention as a promising future aviation technology for next-generation military, space-launch, and transportation vehicles. However, since they require high-temperature combustion of about 2000 K or more, as well as a high flow rate, existing scramjet systems are constructed from a high-temperature metallic material such as Inconel. However, the reliability of its long-term use is very low because of the low melting point in comparison to the combustion temperature [1-4]. Therefore, recent studies have been carried out to improve the stability of combustors for long-term use by applying C/SiC ceramic matrix composites (CMC) materials to a scramjet engine combustor exposed to a high-temperature environment [5].

A regenerative cooling system is typically employed to exchange heat by flowing a coolant such as fuel into the flow path of the wall of a combustor in order to improve the efficiency and durability of the propulsion engine. In such a system, the thermal conductivity of the combustor material is a very important factor in determining the regenerative cooling efficiency. In the case of CMC materials, high-temperature structural stability is superior to that of metallic materials, but it is difficult to obtain excellent efficiency of the

regenerative cooling system because of their low heat conduction characteristics. When CMC materials with high thermal conductivity are utilized as high-temperature components, the cooling system can be effective because it can reduce heat damage due to overheating and maintain the proper temperature [6, 7]. Therefore, further research and development is needed to improve thermal conductivity in order to increase the efficiency of the cooling system of the C/SiC composite materials used in high-temperature environments.

In previous research, the EPD method was used to grow carbon nanotubes (CNTs) on the fiber surface to improve the thermal conductivity of CMC materials. Methods of introducing CNTs into the SiC matrix material have also been studied. In addition, it was reported that the CNT and composite material layers were laminated together to improve the thermal conductivity of the composite material [8-10]. Yoshida et al. attempted to improve thermal conductivity by combining a layer of SiC matrix material with high thermal conductivity and a layer with fibers that contained a material with high thermal conductivity [11]. Feng et al. changed the crystal structure of the fiber and matrix of a material by varying the heat-treatment temperature, thereby improving the thermal conductivity [12]. However, most studies have involved the addition of materials with high thermal conductivity, and studies involving microstructure modification have been performed very rarely. A few studies were carried out with the aim of improving thermal conductivity by altering the fiber volume fraction; however, the thermal conductivity of C/SiC

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composites has been reported to decrease with fiber volume fraction [13].

In the present study, a liquid silicon infiltration (LSI) process has been applied to fabricate C/SiC composites with improved thermal conductivity. This processing technique results in materials with superior thermal conductivity compared with those produced by chemical vapor infiltration (CVI) and polymer infiltration and pyrolysis (PIP); moreover, it has a shorter manufacturing time, easier forming availability, and low manufacturing cost. Microstructure control was induced by surface modification of the carbon fibers with nitric acid solution through a change of bonding strength between the fiber and matrix material. As a result, the small size ($< 10 \mu\text{m}$) of the microcrack area between the fiber and the matrix material decreased and the segment crack area increased, improving the thermal conductivity. In addition, the altered mechanical properties were evaluated and additional analysis was conducted and is reported herein.

Experimental

C/SiC composites

The C/SiC composites were fabricated using the LSI process by the following steps: (1) C/phenol composite material manufacturing process; (2) carbonizing C/phenol composite material in an inert atmosphere to obtain porous C/C; (3) the Si melt was impregnated in a vacuum, at a temperature of 1420°C or higher, with the carbon from phenol resin carbonization to form reacted SiC in the matrix material. In a second process, the phenolic resin shrinks during the carbonization step to generate a large number of internal cracks (segment cracks and microcracks), which act as a passage through which the molten Si is infiltrated by the capillary force in a third LSI process.

The carbon fiber (Pyrofil TM, T300 grade, PAN, Mitsubishi Rayon, Japan) used in this study has a plain weave [0/90] structure. The surface treatment of the fibers was carried out using a nitric acid solution (60%, OCI Company, Republic of Korea) heated to 110°C and held for 1, 5, 15, or 60 min in the solution. The surface-treated fibers were then washed in distilled water and dried at 110°C , and then the fibers were pre-impregnated with phenol resin (KRD-HM2, KOLON INDUSTRIES, Republic of Korea). The prepreps were laminated and cured by vacuum bagging at 180°C to produce fiber-reinforced plastic (FRP). After the carbonization process in a nitrogen atmosphere at 1000°C , the C/SiC composite material was prepared by an LSI process at 1600°C .

Experimental Method

The cross-section of the C/SiC composite was observed with scanning electron microscopy (SEM; S-

4800, HITACH Co., Japan); images were recorded of the surface-treated carbon fiber. Based on the SEM results, the amount of segment cracking and the microcracked area were measured using an image analysis program (Image pro, Media Cybernetics, USA). The density and porosity of the C/SiC composites were measured using Archimedes' method and the three-point bending strength was measured using a material tester (Landmark, MTS, USA) according to the ASTM C1341-13 standard. The bending strength specimen was machined to a size of $1.2 \times 4 \times 45 \text{ mm}$ and measured at room temperature with a span of 40 mm and a crosshead speed of 1 mm/min. The tensile strength of the fibers was measured according to ASTM D3822-07. The fibers were fixed on both sides of paper having a grip area of $30 \times 50 \text{ mm}$, a gauge length of 50 mm, and a crosshead speed of 1 mm/min. The thermal conductivity was measured using a laser flash method (LFA; 467, NETZSCH Co., Germany) with a diameter of 12.7 mm and a thickness of 1.4 mm for the specimen; the measurement was carried out at temperatures of 24.5, 500, 1000, and 1400°C .

Results and Discussion

Fig. 1 shows the thermal conductivity of C/SiC composites based on carbon fibers with different surface treatment times. The C/SiC composites with untreated fibers and those treated for 1 or 5 min showed similar results over the range from room temperature to 1400°C , with conductivities spanning 10.5–11.5 W/m·K. However, in the case of composite specimens with fibers treated for 15 or 60 min, the thermal conductivity increased significantly in proportion to the treatment time. Since the temperature of the LSI process for manufacturing composites is the same for all specimens (1600°C), it is considered that there is no change in the thermal conductivity of the

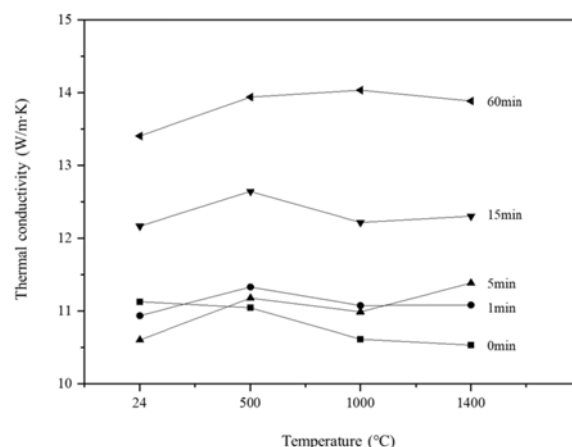


Fig. 1. Thermal conductivity results of C/SiC composites for different fiber treatment times.

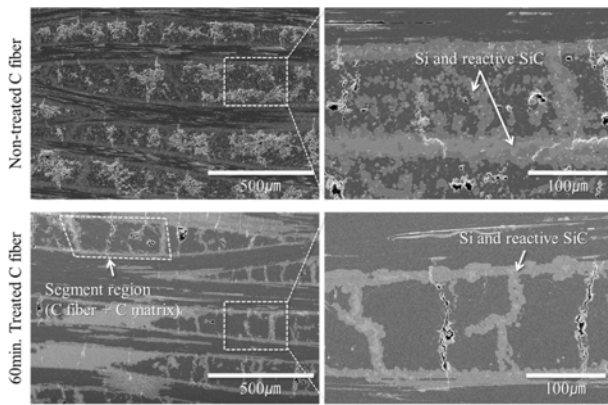


Fig. 2. SEM images of cross-sections of C/SiC composites fabricated using surface-treated C fiber.

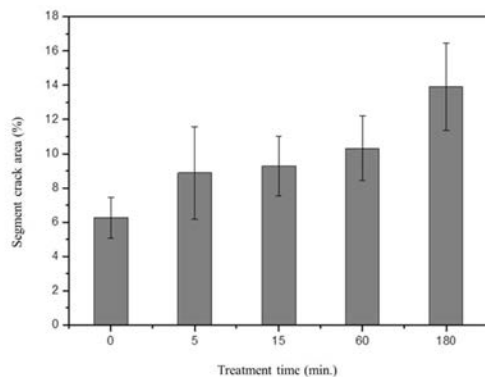
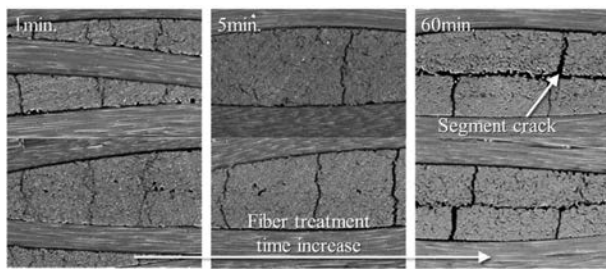


Fig. 3. Segment crack area analysis results for different surface treatment times.

fiber due to the graphitization of the carbon fiber according to the heat treatment temperature. Therefore, it is considered that the thermal properties change due to the difference in internal microstructure among the specimens of the LSI-treated composite material, depending on the surface treatment time of the carbon fiber.

The microstructure was observed in order to confirm the effect of the surface treatment of the reinforcing fiber on the change in thermal conductivity of the C/SiC composite material. The SEM analysis results are shown in Fig. 2, where it can be observed that the C/SiC composites fabricated by the LSI process consist of C/C segment regions, composed of carbon fiber/

carbon materials, and reactive SiC and Si regions surrounding them. In the case of the specimens with untreated fibers, the area of the C/C segment was affected by the infiltration of Si during the LSI process, and it was confirmed that the carbon fiber was damaged. The reason for the infiltration of Si into the inside of the segment region is that a large number of microcracks are generated between single fibers and the matrix during the carbonization process. In addition, large numbers of Si and SiC phases are present in the segment region, and it is considered that these multiple small-scale phases are generated by lowering the thermal conductivity of the entire composite material. However, in the case of specimens subjected to surface treatment for more than 15 min, Si infiltration into the C/C segment region was significantly decreased, and it has been confirmed that the C/C segment region was clearly present. In this case, the formation of Si and SiC phases in the segment region is suppressed and the phase boundaries that obstruct thermal conduction are reduced; as a result, thermal conductivity is improved.

Segment cracking is caused by carbonization shrinkage of the phenolic resin during the carbonization process; this creates the path through which molten Si infiltrates during the LSI process. However, in addition to the segment cracks in the carbonization process, microcracks smaller than the segment cracks may also occur between the single fiber filament and the matrix material in the C/C segment region. The generation of one or the other of these two types of cracks may be favored depending on the bonding force between the fiber and the matrix material, and it is confirmed in this study that the thermal characteristics of the composite material are affected by the presence of different types of cracks. The microcrack is observed adjacent to the reinforcing fiber filament inside the C/C phase, which is responsible for the load transfer of the composite material. Further, the microcracks induce the reaction with molten Si, reinforcing the fiber in the LSI process and causing damage to the fiber, and a reduction in the strength of the composite material is therefore predicted. In the case of FRP with the same fiber volume fraction, the microcrack reduction in the C/C segment of the specimen that has undergone surface fiber treatment leads to an increase in segment cracking, assuming that the shrinkage of the phenolic matrix material occurring during the carbonization step is the same. The changes in the crack patterns were confirmed using automated image analysis, and the results are shown in Fig. 3. The segment cracking area increased from 6% to 14%, depending on fiber surface treatment time, with a concomitant decrease in the number of microcracks inside the C/C segment.

When carbon FRP (CFRP) based on phenolic resin is carbonized at 1000 °C, organic components of the resin are removed and its weight is reduced by about 35%, and about 20% linear shrinkage occurs as shown in

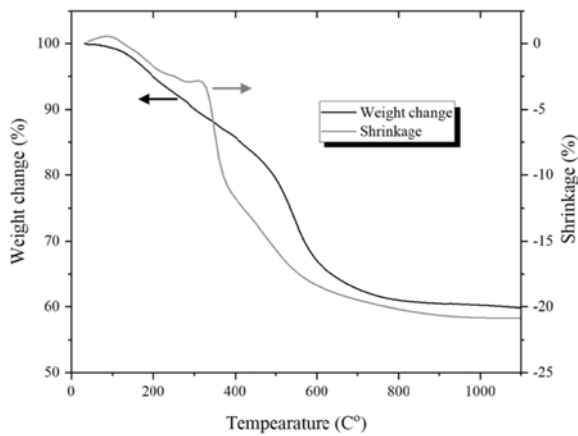


Fig. 4. Density and porosity of C/SiC composites for different fiber treatment times.

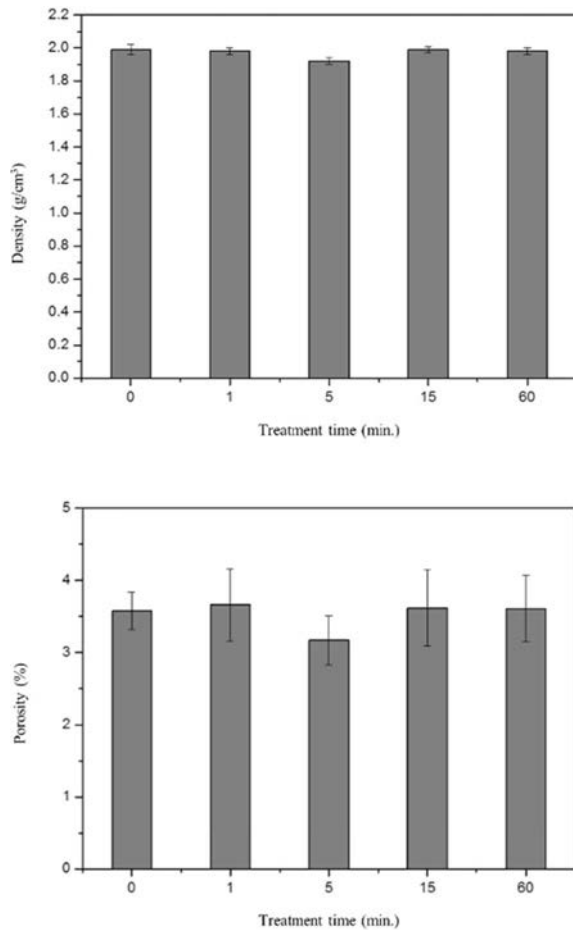


Fig. 5. Flexural strengths of C/SiC composites for different fiber treatment times.

Fig. 4. This shrinkage creates a tensile force on the phenolic resin that is converted to carbon, and creates a debonding force between the fiber and the matrix material. When the bond strength between the fiber and the matrix material is weak, debonding occurs and microcracks occur; in contrast, when the bond strength is higher than a critical value, larger-scale segment

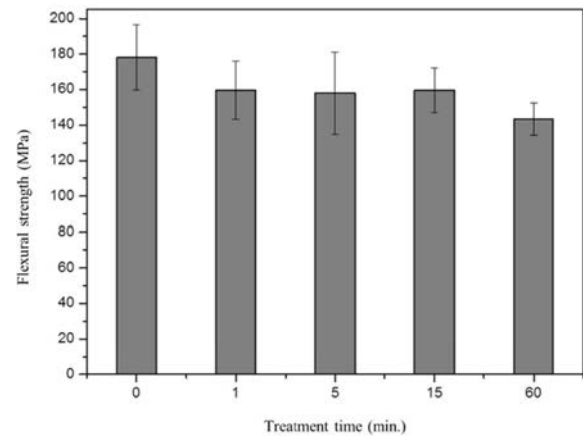


Fig. 6. Tensile strengths of carbon fibers for different surface treatment times.

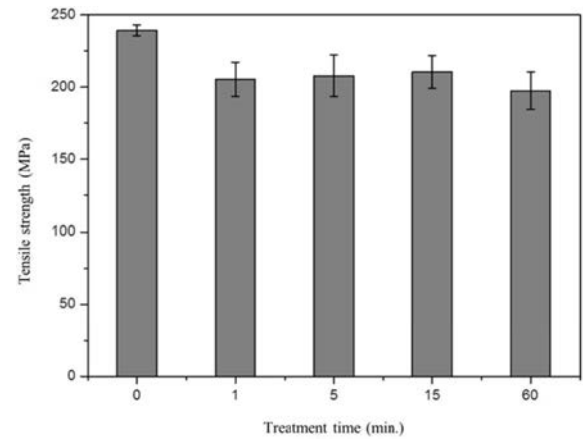


Fig. 7. SEM images of untreated and treated carbon fiber surfaces; treatment durations are overlaid on the images.

cracks are generated.

During treatment of the surface with nitric acid solution in this study, for the 60-min treatment, about 60 $\mu\text{eq/g}$ of acidic functional groups, consisting of carboxyl acid and phenolic acid groups, was formed on the surface. This increase in functional-group density enhances the wettability and absorbency, and increases the surface reaction and bonding between the fiber and substrate [14-18]. This increase in the bonding force is understood to induce the increase in the high-density C/C area and the increase in the segment cracking area around the C/C area by reducing the generation of microcracks between the fiber and the matrix material.

Since the thermal conductivity of the material is determined by the interaction between phonons and scattering, it decreases with increasing number of interfaces. In composite materials, the lower the value of the volume fraction of phases with low thermal conductivity, the lower the conductivity. In order to improve the thermal conductivity of the C/SiC composite fabricated by LSI, a method of suppressing

Si penetration and SiC formation in the C/C regions due to internal microcracks, reducing the volume fraction of carbon fiber, which has relatively low thermal conductivity (SiC: 300 W/m·K, Si: 156 W/m·K, C fiber: 10 W/m·K), needs to be applied. [B] The surface treatment of the fiber has the effect of reducing the number of interfaces in the above two methods. As shown in Fig. 1, thermal conductivity increases with surface treatment time because the amount of microcracks in the C/C segment decreases due to the improvement of the interfacial bonding strength, and the area of larger segment cracks is increased. Therefore, it is considered that the increase of the phonon mean free path, as well as a reduction in scattering occurs, and the number of the interfaces inside the composite material is reduced, thereby improving the heat transfer path [11-12, 19].

Fig. 5 shows the density and porosity of C/SiC composite specimens prepared with different surface treatment times. The density and porosity of C/SiC composites showed similar results, within 2 g/cm³ and 3.6%, respectively, for all specimens, irrespective of the surface treatment time. Therefore, the surface treatment of the carbon fiber did not affect the density and the porosity of the C/SiC composite material, and it was confirmed that the densification was successfully carried out. In general, for C/SiC composite materials, thermal conductivity increases with density because the fraction of SiC matrix material with relatively high thermal conductivity increases [20]. In this study, improvement of thermal conductivity was attempted without increasing density or altering the fiber volume fraction, and the improved conductivity results were instead obtained by surface treatment of the fibers.

Fig. 6 shows the three-point bending strengths of the C/SiC composites. Bending strength is predicted to increase with the increase of the fiber surface treatment time because the carbon fiber damage due to Si infiltration into C/C segment is reduced by formation of high-density C/C regions without microcracking. However, as seen in Fig. 5, the bending strength tends to decrease from 178 to 143 MPa with treatment time. It is therefore concluded that the decrease of the strength of the composite material is affected by the properties of the reinforced carbon fibers. In order to confirm this, tensile strength testing of each surface-treated fiber was undertaken. For the carbon fibers treated with nitric acid, the tensile strength of the fiber is observed to decrease from 239 to 198 GPa; these results are presented in Fig. 7.

A reduction in the strength of carbon fibers is known to occur when the fiber surface is damaged or if its roughness is increased. This was confirmed by Itoi et al. who found that nitric acid treatment generated pitted and fragmented surfaces, resulting in mechanical properties that were reduced by more than 15% [16]. This phenomenon was also confirmed in the present

study, and Fig. 8 shows the SEM analysis results after fiber surface treatment. Pitting and surface damage, which were not observed on the surface of the untreated fiber, were observed to a degree that is dependent on the duration of the nitric acid treatment; these surface structure alterations are considered to be a cause of the mechanical property deterioration, observed as the decrease in the tensile strength of the fiber, which increased with the nitric acid treatment time [15, 21].

Pits and crevasses are generally present on the surface of the fiber, created during nitric acid treatment; this phenomenon has also been confirmed in this study. In addition, high-modulus carbon fibers have large crystals and large basal planes; therefore, the number of edge, corner lateral planes, and voids is reduced with respect to that of low-modulus carbon fibers. For this reason, changes due to acidic treatment are known to be reduced. The carbon fiber used in this study is low-modulus carbon fiber, and it is considered that the fiber damage or the characteristic change due to nitric acid is obviously well expressed [16].

As described above, the change of chemical and surface morphology of carbon fiber by nitric acid treatment has a great influence on the production of carbon fiber/phenol composite material, which is an early stage of the CMC manufacturing process. The increase in the roughness of the fiber surface by nitric acid treatment improves the bonding strength between the fiber and the phenolic resin, and the active groups on the fiber surface improves the wettability between the liquid phenolic resin and the fiber, thereby increasing the bonding strength between the fiber and the phenolic resin. This increase in bonding strength was confirmed by the study of Li et al. in which increased interfacial shear strength and reduced carbon fiber wetting angle of nitrate surface-treated carbon FRP was observed [22].

The increase of the bonding strength between the carbon fiber and phenol resin has a great influence on the cracking behavior during the carbonization step. In the carbonization step, the bonding between the untreated fiber and the carbonized phenol resin is via very weak van der Waals forces, and is easily debonded to form a large number of microcracks. However, the mechanical bonding by the surface roughness is thought to prevent debonding with the carbon matrix material, thereby suppressing the generation of microcracks. It can be concluded that the thermal conductivity of the final composite material is improved due to the alteration of the cracking pattern of the carbonized composite due to fiber surface treatment which changes the formation pattern of the SiC and Si matrix during the subsequent LSI process.

Conclusions

In this study, the microstructure of C/SiC composites was controlled to improve thermal conductivity and mechanical properties. Nitric acid surface treatment of carbon fiber samples improved the bond strength between the fiber and the base metal, thereby controlling microcrack formation during the manufacturing process and inducing changes in the microstructure of the final composite material. The surface treatment induced chemical/morphological changes in the fiber surface, and the LSI-processed C/SiC composite material was fabricated from these fibers. As the fiber surface treatment time increased, the thermal conductivity tended to increase rapidly, with the segment crack area inside the C/SiC composite increasing from 6.28 to 10.31% after 15 min of treatment. In other words, thermal conductivity was improved by increasing the larger-scale segment cracking due to suppression of microcrack formation; this result was confirmed as the cause of an increase of the bonding strength between the fiber and the matrix, via the treatment of the fiber surface. However, we also observed that mechanical properties tend to decline due to surface damage (pits and crevasses) of the fiber during the surface treatment. This effect can be minimized by deducing appropriate surface treatment times for the fibers.

In this study, the technology to change thermal conduction characteristics in LSI-processed C/SiC composite materials without changing the fiber volume fraction and density has been investigated, and the conditions that can minimize the deterioration of mechanical properties through appropriate surface treatment time have also been derived.

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