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Examination of strength-controlling factors in C/C composites using bundle composites

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Abstract—C/C composites unidirectionally reinforced by one fiber bundle (the bundle C/C composites) were fabricated and tested in tension. Through the comparison between the tensile strength of the bundle C/C composite and that of the laminated one, effects of lamination on the tensile strength of the C/C composites were examined. Results suggested that defects in the laminae, such as transverse cracks, have no effects on the tensile strength of the C/C composites. This means the strength-controlling factors are included in the bundle. As one of the factors in the bundle, the effect of bonding strength of fiber/matrix interface was examined by using the fiber bundles with different surface treatments. In addition to surface oxidized and non-oxidized fiber bundles, an attempt was made to form porous carbon coating layers around the fibers to reduce the bonding strength intentionally. Results suggested that the bonding strength of the fiber/matrix interface, which was evaluated by bundle push-out tests, have significant effect on the tensile strength of C/C composites. It was also shown that the porous coating layers were effective in improving the tensile strength of C/C composites.

Keywords: C/C composites; tensile strength; surface treatment; interface.

1. INTRODUCTION

Improvement in the mechanical properties of carbon–carbon (C/C) composites is of considerable importance, as these composites are finding applications requiring them to be strong and tough but lightweight at extremely high tempera-

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tures. The interest of aerospace industries in the composites as turbine systems, rocket-propulsion components, and heat shields of reentry vehicles has rapidly increased [1]. Therefore extensive research has been carried out to evaluate and improve the mechanical properties of the C/C composites. In these researches, one of the major issues has been clarifying factors controlling the strength of the C/C composites, because the tensile strength of C/C composites is usually 30–40% of that estimated from the rule of mixture, although almost 100% is achieved in CFRPs [2, 3]. This means that the tensile strength of C/C composites will be drastically improved if the strength-controlling factors are made clear.

There are several possible factors that could affect the strength, which are roughly divided into two categories. One includes interactions between the laminae. For example, cross-ply C/C composites include a large number of transverse cracks as shown in Fig. 1 (indicated by arrows). The laminated C/C composites may also include inter-laminar cracks. Those cracks possibly degrade the strength of the C/C composites. Thermal residual stresses between the laminae could be another factor in degradation. Geometrical factors, such as waviness of the fiber bundles, may also be expected to be strength degradation factors. The other factors are in the bundle, which are voids, bonding strength of fiber/matrix interface, and fiber alignment in the bundle, etc. At present, however, it is not clear which factors have greatest influence on the strength of the C/C composites.

In this paper, the interactions between the laminae were examined first by comparing the strength of the cross-ply laminated C/C composites with that of C/C composites unidirectionally reinforced by one carbon fiber bundle (the bundle C/C

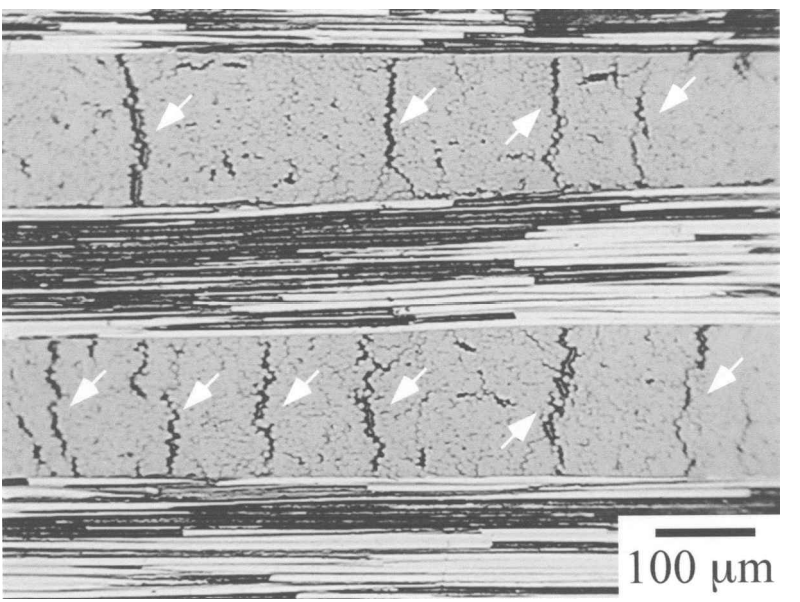


Figure 1. Cross-sectional view of cross-ply C/C composite.

composite). In the next step, the effect of the interface was examined as one of the factors inside the bundle by changing the surface treatment of the carbon fibers.

2. FABRICATION OF BUNDLE C/C COMPOSITE SPECIMENS

Reinforcements used for the bundle C/C composites are high strength type PAN-based carbon fiber bundles (IM-600, 6000 filaments, Toho Tenax Co., Japan), which possess two different surface types. One was oxidation-treated surface *(treated)* and the other a non-oxidized one *(untreated).* The oxidation treatment is usually applied to enhance the bonding of the fiber/matrix interface in CFRPs. Phenolic resin (PR-9480, Sumitomo Bakelite Co., Japan) was used as a row material of the matrix. Material properties of the carbon fiber are summarized in Table 1 [4].

In the processing of the bundle composites, a fiber bundle was dipped in phenolic resin with 20 wt% of acetone, and subsequently evacuated for 20 min. Then, the bundle was pulled up at a constant speed of 5 mm/s and went through a die with a hole (0.7 mm in diameter) to control the shape of the cross-section and to remove excess resin. After keeping at room temperature for 24 h, the bundle was cured at 453 K for 5 h to obtain a CFRP (the bundle CFRP). Then, it was carbonized at 873 K in N_2 atmosphere to obtain the bundle C/C composites (the 873 K bundle C/C composite). Part of the specimens was successively heat treated at 2073 K to enhance carbonization (the 2073 K bundle C/C composite).

Cross-sectional views of the bundle composites are shown in Fig. 2. As shown in Fig. 2a and d, the cross-section of the bundle CFRP is almost circular and no voids are observed even in the magnified view. Volume fraction of the carbon fibers (V_f) was measured by image processing on the magnified view. It was about 50% in the bundle CFRP. After the heat treatments, the shape of the cross-section was changed due to inhomogeneous shrinkage during carbonization (Fig. 2b, e). Although cracks in the matrix also increased with increasing heat treatment temperature, the carbon matrix was relatively dense even without re-impregnation, as shown in Fig. 2c, f. This may be because the constraint on shrinkage during carbonization in the bundle C/C composites is smaller than that in the laminated C/C composites, which require several re-impregnations to get sufficient density. The resulting V_f in the bundle C/C composites was 58% at 873 K and 64% at 2073 K.

Cross-ply laminated C/C composites were also prepared for comparison, row materials of which were the same as the bundle composites. A conventional

Table 1.
Materials properties of carbon fiber (IM600)

	Average tensile strength (MPa)	Young's modulus (GPa)	Failure strain (%)	Average fiber diameter (μm)
IM600-6K	5690	285	2.0	5

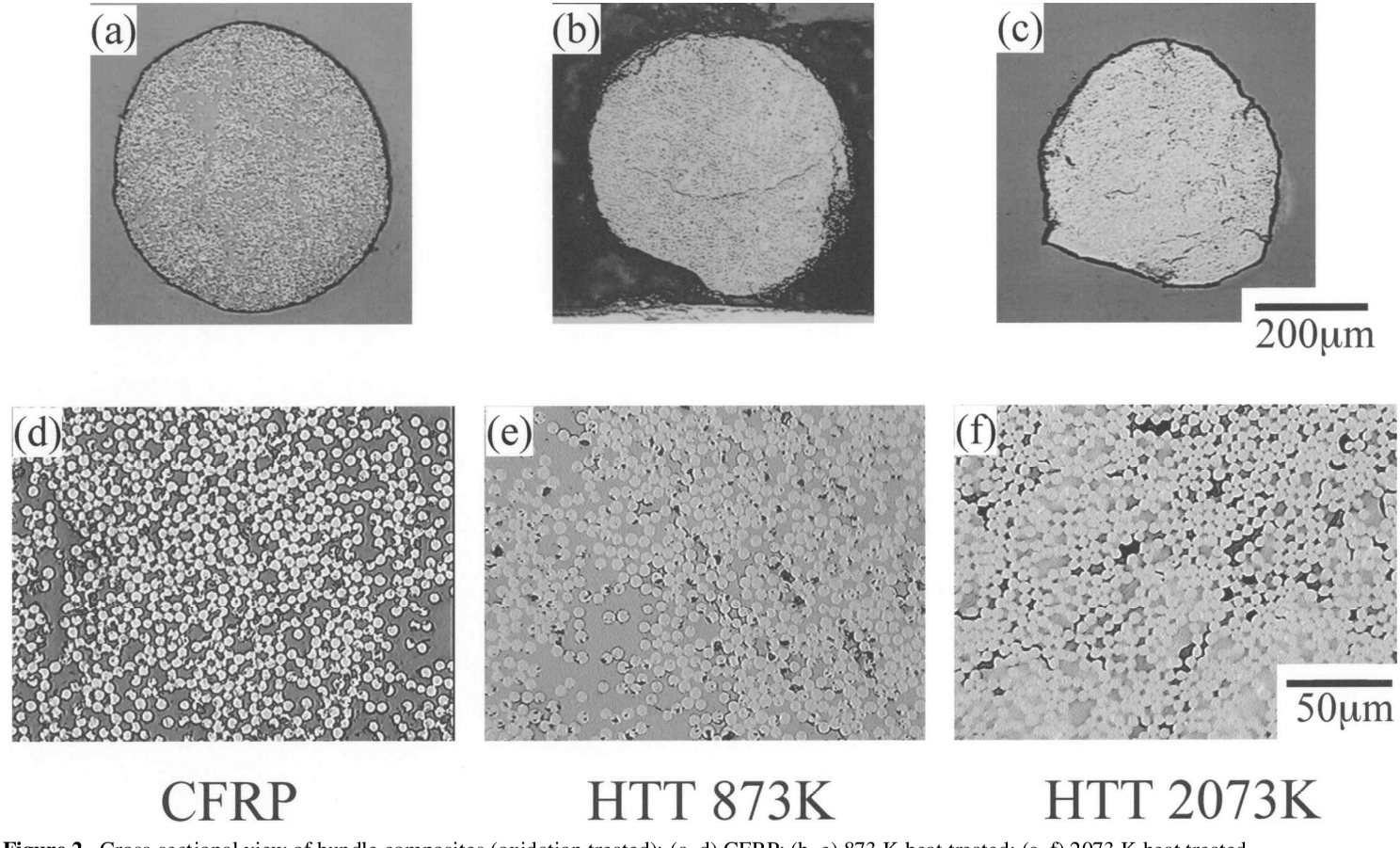


Figure 2. Cross-sectional view of bundle composites (oxidation treated): (a, d) CFRP; (b, e) 873 K heat treated; (c, f) 2073 K heat treated.

resin-char process was used with the final heat treatment temperature at 2273 K. Impregnation of phenolic resin and a heat treatment were repeated 6 times to densify the carbon matrix. The resulting V_f was about 62%, which was almost the same as the 2073 K bundle C/C composites. The cross-sectional view was already shown in Fig. 1, which includes a large number of transverse cracks.

3. EFFECT OF LAMINATION ON TENSILE STRENGTH

3.1. Tensile test

Tensile tests were carried out on the bundle CFRPs and the bundle C/C composites heat-treated at two different temperatures. The cross-ply laminated C/C composites were also tested for comparison. All the tensile tests were carried out at room temperature, and crosshead speed was set to 0. 1 mm/min.

Figure 3 shows geometries of the tensile test specimens. As shown in Fig. 2a, steel tube tabs were attached on both ends of the bundle composite using expanding cement. For the cross-ply laminated C/C specimens, aluminum tabs were attached as shown in Fig. 2b. In the tensile tests, strain was measured by a non-contact type extensionmeter equipped with two CCD cameras and an image processing system.

In most cases, test results of the bundle C/C composites were indicated by the fiber efficiency (Y) defined by the following equation:

$$Y = \frac{P_{\text{exp}}}{n\sigma_{\text{f}}^{\text{ave}} S_{\text{f}}} \times 100\ (\%), \tag{1}$$

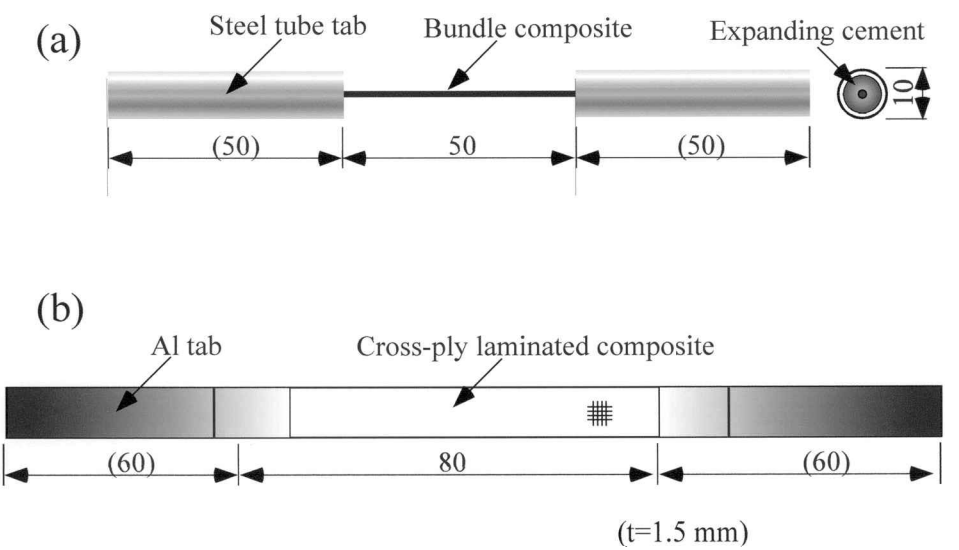


Figure 3. Geometries of tensile test specimen (a) bundle composites, (b) laminated composites.

where P_{exp} is the maximum load obtained by the tensile test, n is the number of filaments in a bundle, σ_f^{ave} is the average tensile strength of the fiber, and S_f is the average cross-sectional area of the fiber. These properties are listed in Table 1. In some case, the cross-sectional areas of the bundle composites were measured after tensile tests to obtain stress–strain curves and Young's moduli.

In the case of the cross-ply laminated C/C composites, the fiber efficiency was calculated as follows:

$$Y = \frac{\sigma_C^{exp}}{\sigma_f^{ave} V_f^0}, \tag{2}$$

where σ_C^{exp} is the tensile strength obtained by the experiment, σ_f^{ave} is the average tensile strength of the fiber, and V_f^0 is the fiber volume fraction in the testing direction.

3.2. Results and discussion

Figure 4 shows typical stress–strain curves of the bundle composites. All specimens showed linear relation up to the final fracture. Young's modulus of the CFRP was 135 GPa, which agrees closely with that estimated from the rule of mixture. In the case of the C/C composites, Young's moduli for C/C composites were around 160 GPa and were slightly higher in the specimen with higher heat treatment temperature. Increase in the Young's modulus in C/C composites might be due to increase in the volume fraction and carbonization of the matrix.

A major difference in the bundle composites was the fiber efficiency (Y), as summarized in Fig. 5. The fiber efficiency of the bundle CFRPs with the surface-

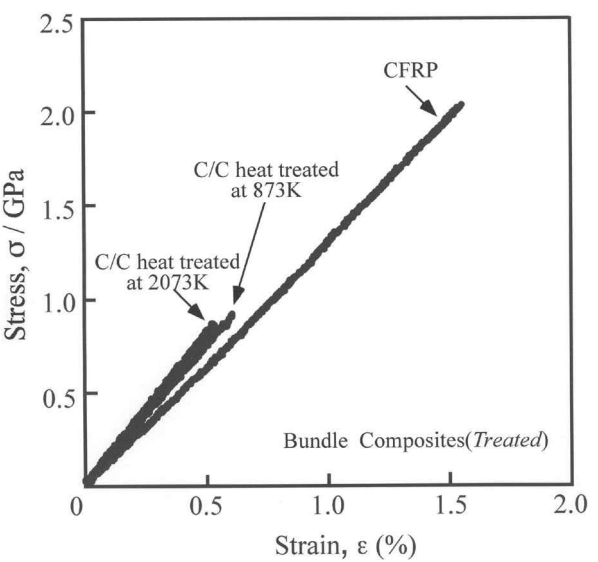


Figure 4. Stress–strain curves of bundle composites tested in tension at room temperature.

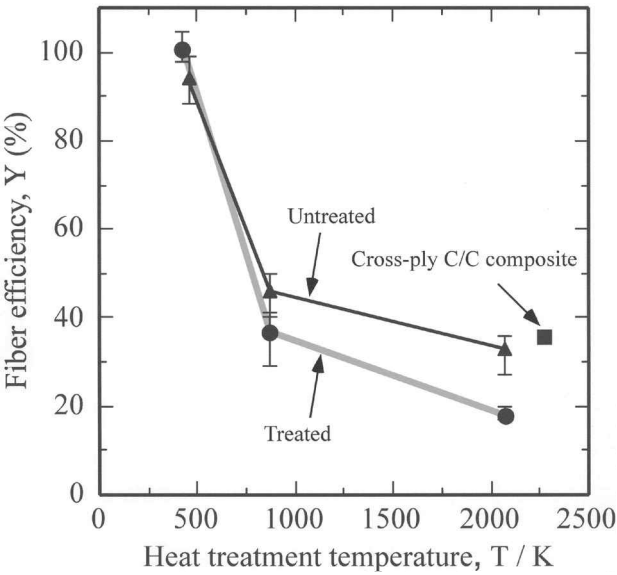


Figure 5. Fiber efficiencies of bundle composites tested in tension at room temperature.

oxidized carbon fibers (the treated bundle C/C composite) and the non-oxidized carbon fibers (the untreated bundle C/C composite) showed nearly 100% and 93%, respectively. The slight difference must correspond to the difference in the bonding strength of the fiber/matrix interface due to the surface treatments as mentioned before. These results suggest that the process employed in this study can provide the bundle composites with enough mechanical properties without fiber damage during processing.

In the 873 K bundle C/C composites, the fiber efficiencies of the treated and the untreated composites were degraded to 37% and 46%, respectively. Further degradation was observed in the 2073 K bundle C/C composites, which showed fiber efficiencies of 18% for the treated C/C composites and 34% for the untreated ones. It is noted that the fiber efficiency of the untreated 2073 K C/C composites showed almost the same value as that of the cross-ply laminated C/C composites, shown as a solid square in the figure. These results suggest that the tensile strength of the C/C composites is insensitive to the factors relating to the interaction between the laminae. In other words, the tensile strength of C/C composites is affected mainly by the factors inside the bundle.

To examine the difference between the treated and the untreated C/C composites, fracture appearances were observed by SEM as shown in Fig. 6. The fracture appearance of the untreated CFRPs shown in Fig. 6b is more fibrous compared with that of the treated ones shown in Fig. 6a. The difference must correspond to the difference in the bonding strength at the fiber/matrix interface. In the case of the bundle C/C composites, though the difference in the fracture appearance is not clear for the 873 K C/C composites as shown in Fig. 6c and d, quite different

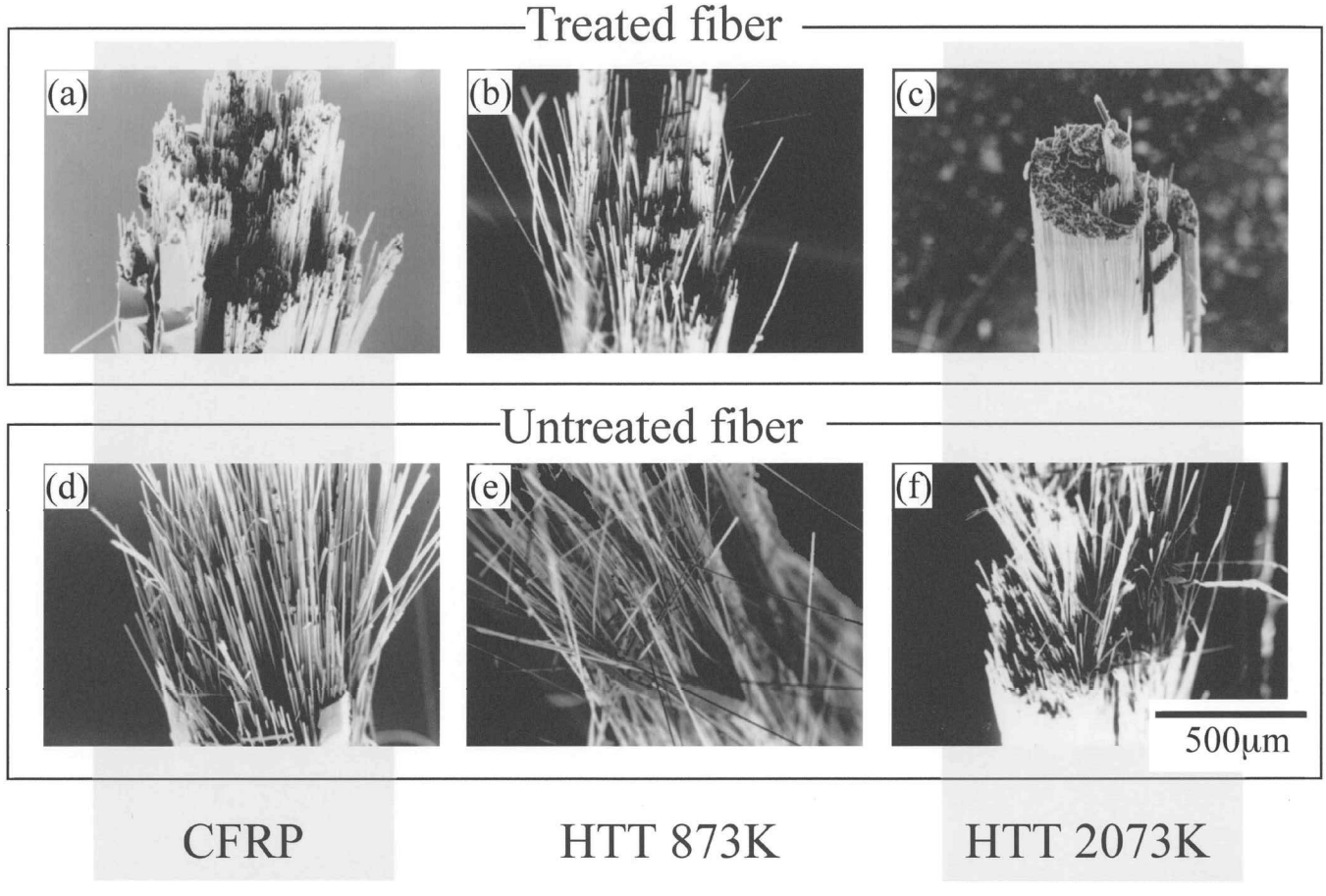


Figure 6. Fracture appearances of bundle composites tested in tension at room temperature: (a–c) surface treated; (d–f) untreated; (a, d) CFRP; (b, e) 873 K heat treated; (c, f) 2073 K heat treated.

appearances were observed in the 2073 K C/C composites. As shown in Fig. 6e, the treated C/C composites showed a flat fracture surface. On the other hand, fibrous fracture appearance was observed in the untreated C/C composites as shown in Fig. 6f.

Generally speaking, the flat and fibrous fracture appearances in brittle matrix composites are considered to originate from strong and weak fiber/matrix interfaces, respectively [5]. In the case of the strong interface, matrix cracks, which will initiate prior to the fiber fracture, propagate across the fibers without debonding at the fiber/matrix interface. On the other hand, the weak interface will arrest matrix cracks by the debonding. The resulting tensile strengths are considered to be higher in the composites with the weak interface than those with the strong one. Since the tendency of the strength agreed with the behavior mentioned above, the bonding of the interface is expected to be strong in the treated C/C composites and weak in the untreated C/C composites.

4. EFFECT OF INTERFACE STRENGTH ON TENSILE STRENGTH

In the previous section, it was concluded that the major controlling factors of the tensile strength in the C/C composites exist inside the bundle. It was also expected that the weak interface improves the tensile strength. For the quantitative understanding of such behavior, the bonding strength of the fiber/matrix interface was measured on each bundle composite to evaluate the relation to the tensile strength. In addition, an attempt was made to reduce the bonding strength of the interface intentionally by forming a porous carbon coating layer around the fibers.

4.1. Experimental procedure

4.1.1. Materials. Reinforcements used in this section were high modulus type PAN-based carbon fiber bundles (UM-46 12000 filaments, Toho Tenax Co., Japan) due to the material preparation. Materials properties were listed in Table 2 [4]. They also have two types of surfaces, which are oxidation treated and untreated. The processing of the bundle composites was the same as that in the previous section. The resulting volume fraction was 50%, 57%, and 63% for the bundle CFRP, the 873 K and the 2073 K C/C composites, respectively.

In some specimens, the carbon fiber bundles were coated by bismaleimide-triazine (BT) resin prior to the bundle processing to reduce the bonding strength of the

Table 2.
Materials properties of carbon fiber (UM46)

	Average tensile strength (MPa)	Young's modulus (GPa)	Failure strain (%)	Average fiber diameter (μm)
UM46-12K	4705	435	1.1	4.7

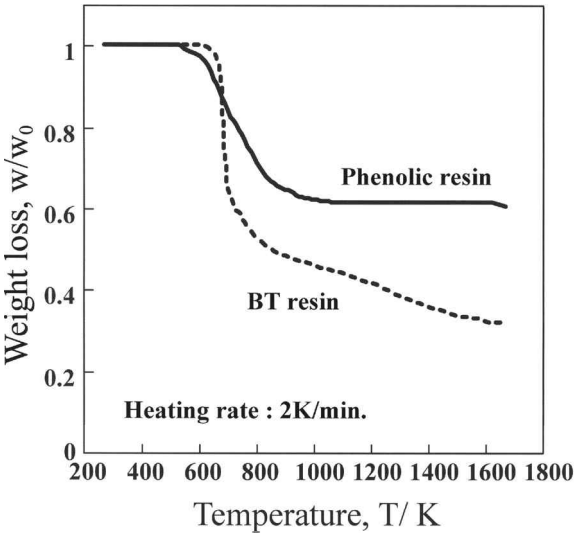


Figure 7. Thermo-gravimetric analyses of phenolic and BT resin.

fiber/matrix interface. Since BT resin yields a smaller amount of carbon when it is carbonized, a porous carbon layer is expected to be formed around the fibers. Actually, thermo-gravimetric analyses in Ar atmosphere revealed that the carbon yield of BT resin at 873 K was 48%, which was smaller than that of phenolic resin (66%) as shown in Fig. 7. In the coating process, a carbon fiber bundle was dipped in a solution of BT resin (0.25 wt%) in l-methyl-2-pyrrolidone, and they were evacuated for 20 min. The untreated carbon fiber bundles were used for the BT resin coated specimens, and the heat treatment temperature was set at 873 K.

All the tensile tests were carried out at room temperature, and crosshead speed was set to 0.1 mm/min.

4.1.2. Bundle push-out test. The interfacial shear strength was evaluated to examine the relation to the tensile strength of the C/C composites by bundle push-out tests. Although push-out or push-in tests on a fiber in a composite are usually carried out using a micro-Vickers hardness indenter [6], our preliminary experiments revealed that the indenter contacted carbon matrix before applying a sufficient load to push-in or push-out the carbon fiber. To avoid such difficulty, the bundle push-out test was employed in the present study to obtain *relative* interfacial shear strengths (τ_i). Figure 8 shows a schematic view of the bundle push-out test. In the preparation of the specimen, the bundle C/C composite was inserted in an alumina tube with highly viscous adhesive. Then, the specimen was mounted in plastic, and it was sliced by a diamond wheel. The sliced specimen was polished to make the specimen thickness around 200 μm. The thickness of the specimen was determined from the maximum compressive stress during the push-out tests, which should be lower than the fracture stress of the carbon fiber.

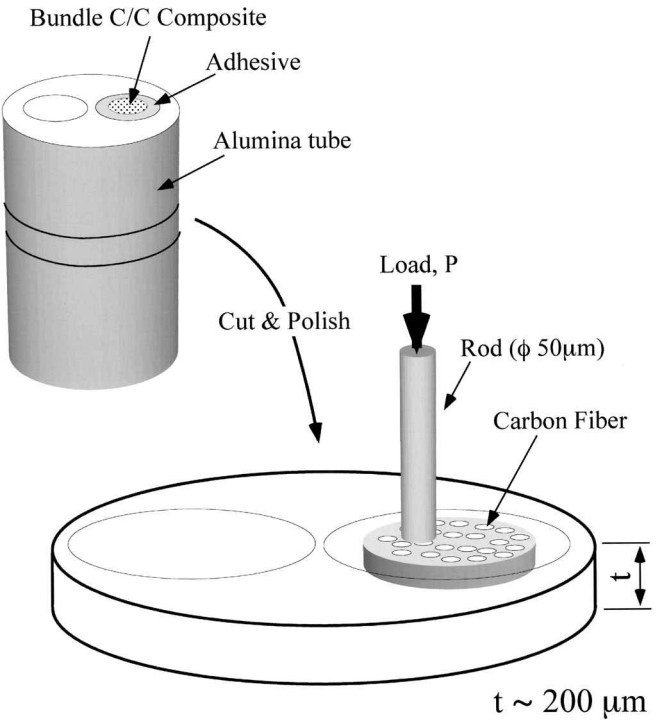


Figure 8. Schematic illustration of bundle push-out test.

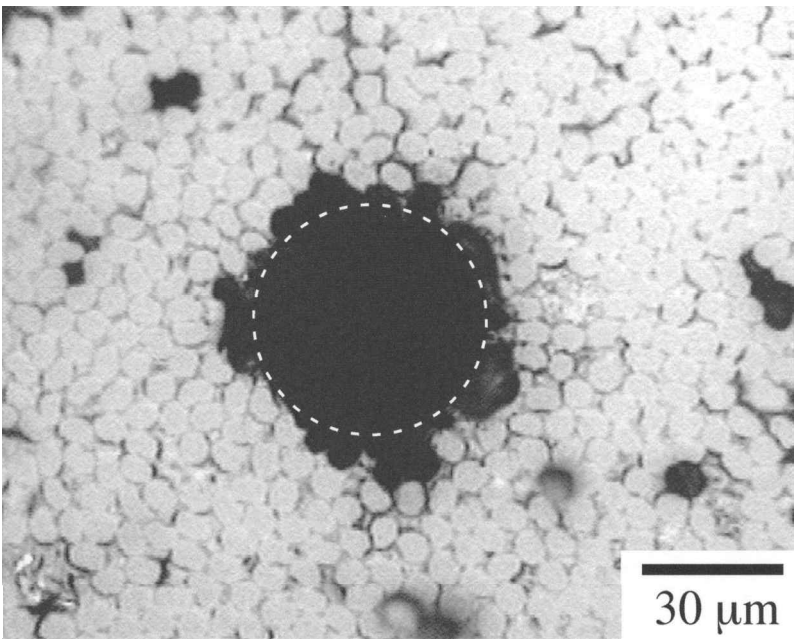
In the bundle push-out test, the specimen was set on the steel plate with a hole (70 μm in diameter), and was loaded by the rod (50 μm in diameter) made of tungsten carbide attached on the tensile testing machine. To check the validity of the experiment, the specimen was observed by an optical microscope after the bundle push-out test. Figure 9a shows a typical specimen surface after the bundle push-out test. Several fibers were successfully pushed out along with the carbon matrix without compressive fracture of the fibers or the buckling of the pushed-out C/C rod. Through the comparison between the diameter of the rod, shown by the dashed circle, and that of the hole made on the C/C composite, the fibers on the edge of the rod seemed to be pushed out. Because of this, we roughly assumed that the actual circumferential length of the hole was almost 1.5 times larger than the diameter of the rod as schematically shown in Fig 9b. Then, the *relative* interfacial shear strength (τ_i) was calculated by the following equation:

$$\tau_i = P/3\pi r, \tag{3}$$

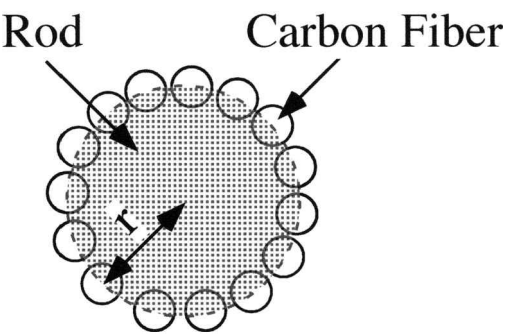
where P is the maximum load, and r is the radius of the rod.

4.2. Results and discussion

Figure 10 shows typical stress–strain curves of the BT coated and the un-coated C/C composites (the heat treatment temperature was 873 K), which are linear up to



(a)



(b)

Figure 9. Top view of specimen surface after push-out test: (a) micrograph, (b) schematic illustration.

the final fracture. As compared in the figure, Young's moduli for both specimens are almost the same value with that estimated from rule of mixture of 252 GPa by assuming Young's modulus of matrix as 10 GPa. This means that the bundle C/C composites were successfully fabricated even with the BT coating. The fiber efficiencies of the bundle composites were summarized in Fig. 11. The tendencies of the treated and the untreated C/C composites were similar to the results in the previous section. In the case of the BT coated composites, the fiber efficiency of the bundle CFRP was the lowest, though the difference was small. In comparison, the BT coated C/C composites showed the highest fiber efficiency of 56% with the heat treatment at 873 K.

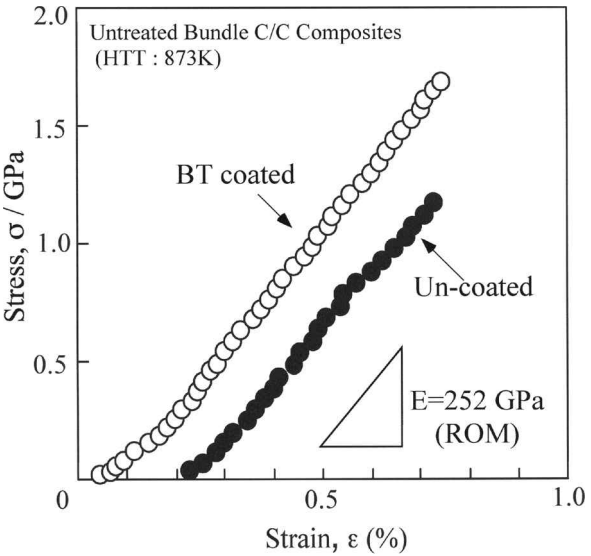


Figure 10. Stress–strain curves of bundle C/C composites tested in tension at room temperature.

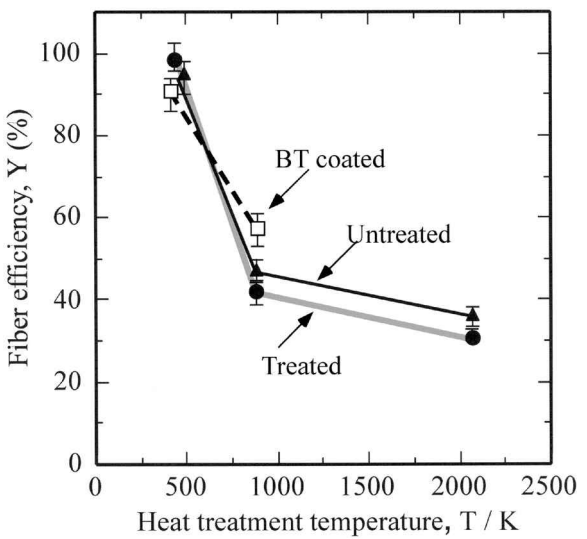


Figure 11. Fiber efficiencies of bundle composites tested in tension at room temperature.

Corresponding interfacial shear strength was obtained by the bundle push-out tests. Figure 12 shows a typical load–displacement curve of the bundle push-out test. Although the tendency was not so clear due to the low resolution of the displacement measurements, the maximum load was observed at the displacement around 1.5 μm, followed by gradual decrease. The *relative* interfacial shear strengths (τ_i) were plotted in Fig. 13. Although the scatter of the τ_i is relatively large, it was clearly indicated that τ_i decreases with increasing fiber efficiency. It is

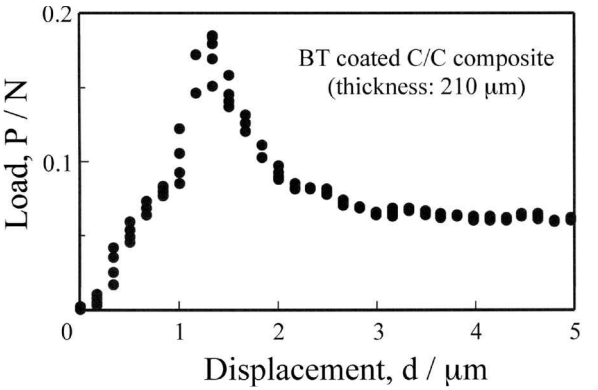


Figure 12. Load–displacement curve of bundle push-out test.

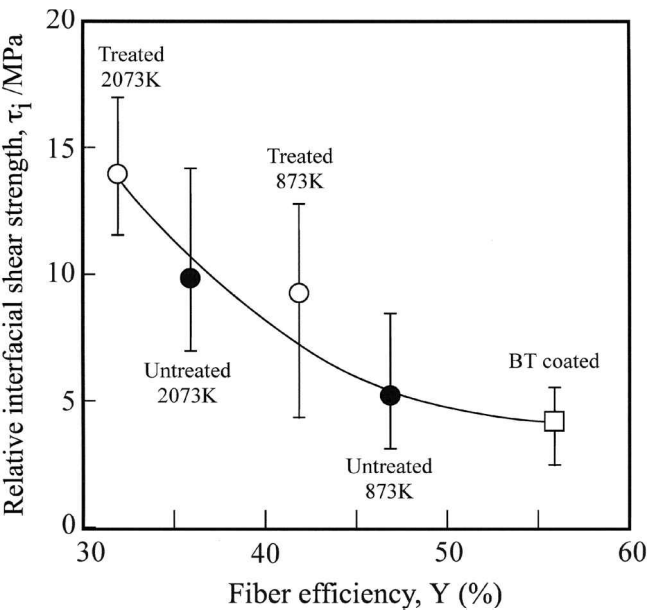


Figure 13. Relation between fiber efficiency and relative interfacial shear strength.

noted that the interfacial shear strength was successfully reduced by the BT coating, and the strength was improved up to 56%.

The dry bundle strength would be one measure of potential strength of C/C composites. It was shown by the following equation [7]:

$$\frac{\sigma_b}{\sigma} = \left(\frac{1}{me}\right)^{1/m} \frac{1}{\Gamma(1+1/m)}, \tag{4}$$

where σ_b is the dry bundle strength, σ is average strength of the fiber, m is Weibull's modulus, and Γ is the gamma function. Therefore, σ_b/σ can be compared with the

fiber efficiency obtained in this experiment. Since Weibull's modulus for the fiber in these experiments is approximately 5.5, σ_b/σ is calculated as 0.66, which suggests that further improvement in the tensile strength would be possible by reducing the strength of the interfacial shear strength.

Another possible indication would be a theory for the strength of brittle matrix composites assuming a global load sharing condition, shown by the following equation [8]:

$$\sigma_u = f\sigma_c\left(\frac{2}{m+2}\right)^{1/(m+1)}\frac{m+1}{m+2}, \tag{5}$$

where σ_u is a tensile strength of the composite, f is a fiber volume fraction, m is Weibull's modulus, and σ_c is shown by the following equation:

$$\sigma_c = \left(\frac{\sigma_0^m \tau L_0}{r}\right)^{1/(m+1)}, \tag{6}$$

where σ_u is an average strength of a fiber (with radius r) at gauge length of L_0. τ is factional sliding resistance at the fiber/matrix interface, which is expected to have a correlation with τ_i. The theory, however, predicts that the tensile strength of the composite will increase with increasing τ, which is the opposite behavior to that in the present experiments. Since the theory well predicts the behavior of ceramic matrix composites, there must be other controlling factors in the strength of the C/C composites besides interfacial strength that have not yet been taken into account. Further studies are required to clarify the behavior of the C/C composites.

5. CONCLUSION

A comparative study on the tensile strength of the bundle C/C composites and the cross-ply laminated C/C composites was conducted. The effect of the interfacial shear strength on the tensile strength of C/C composites was also examined. Through these experiments, the following conclusions were reached:

(1) The strength of the C/C composites is insensitive to the interactions between the laminae, such as transverse cracks. This means that the strength-controlling factors are in the bundle.

(2) The bonding strength at the fiber/matrix interface was one of the important stress-controlling factors to improve the tensile strength of the C/C composites, although there must be other factors.

(3) The BT coating applied on the carbon fibers successfully reduced the bonding strength at the fiber/matrix interface, and improved the tensile strength of the C/C composites.

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